Chapter 8
Biofuels for Transport: Prospects and Challenges

Rafael Luque, Sara Pinzi, Juan M. Campelo, Juan J. Ruiz, Iosvani Lopez, Diego Luna, Jose M. Marinas, Antonio A. Romero, and M. Pilar Dorado

Abstract Environmental issues, the growing demand for energy, political concerns and the medium-term depletion of petroleum created the need for the development of sustainable technologies based on renewable raw materials. The so-called biofuels might help to meet the future energy supply demands as well as contributing to a reduction of green house gases emissions. In this work, we aim to provide the latest update of the production and potential of biofuels in the transport sector including type of biofuel, feedstocks and technologies as well as some realistic engine tests for the widespread use of biofuels in our society.

Keywords First generation biofuels · Biodiesel · Biogas · Bioethanol · Biobutanol · Second generation biofuels · Synthetic fuels · Engine performance · Emissions

8.1 Introduction

There is now a general scientific consensus that observed trends in global warming are been caused by fossil-fuel combustion and anthropogenic emissions of greenhouse gases (GHG) including nitrous oxide (N_2O) and specially carbon dioxide (CO_2) and methane (CH_4) [1]. Initial concerns about the impact of GHG in our society led to the development of the United Nations Framework Convention on Climate Change (1992) which in turn resulted in the 1997 Kyoto Protocol as a way to tackle the problem. In 2002 the European Union ratified the Kyoto Protocol and emphasised the potential for scientific innovation as a means of countering GHG emissions. Neither these targets nor the Kyoto targets have so far been met. However, judging from the figures of energy consumption over the last few years, the current scenario is believed to complicate in the future. Transport has shown the

---

R. Luque (✉)
Departamento de Química Orgánica, Universidad de Córdoba, Campus de Rabanales,
Edificio Marie Curie (C3), E-14014, Córdoba, Spain
e-mail: q62alsor@uco.es

V. Shah (ed.), *Emerging Environmental Technologies*,
DOI 10.1007/978-90-481-3352-9_8, © Springer Science+Business Media B.V. 2010

highest rates of growth in GHG emissions in any sector over the last ten years (20% global CO_2 emissions, 25% UK emissions), with a predictable 80% higher energy use and carbon emissions than now by 2030 [2].

Oil is the world's primary source of energy and chemicals with a current demand of about 12 million tonnes per day (84 million barrels a day) [3] and a projection to increase to 16 million tonnes per day (116 million barrels a day) by 2030. While a 30% of the global oil consumption accounts for transport, a striking 60% of the rising demand expected for 2030 corresponds to transport [4]. With the transport sector expanding in the US and Europe and specially developing in the newly industrialised and emerging economies of China and India, these values can easily be underestimated. The availability of conventional oil is again becoming geographically restricted and a general agreement now is that the era of cheap and secure oil (cheap energy) is over [5, 6]. Several alternatives are currently been explored, including a range of carbon free and renewable sources (photovoltaics, wind and nuclear power, hydrogen), in an attempt to replace natural gas, coal and oil in the electricity generation sector. However there is not such equivalent in transportation yet, since fuel cells, electric/hydrids and natural gas based cars are still a long way from becoming mainstream vehicles.

A short and medium term alternative is needed. Crop-based fuels denoted as biofuels including biodiesel and bioethanol, emerged as a real alternative to the use of gasoline and conventional diesel in transportation. There has been a relatively high acceptance from general public, governments, producers and part of the agricultural sectors in promoting the expansion of biofuels in our society in an attempt to switch from the petrol-based industry we have been relying on for the last 50+ years to a biobased industry and society that can guarantee a more secure energy supply. An exponential increase in the consumption of these biofuels has taken place in the last few years (Fig. 8.1).

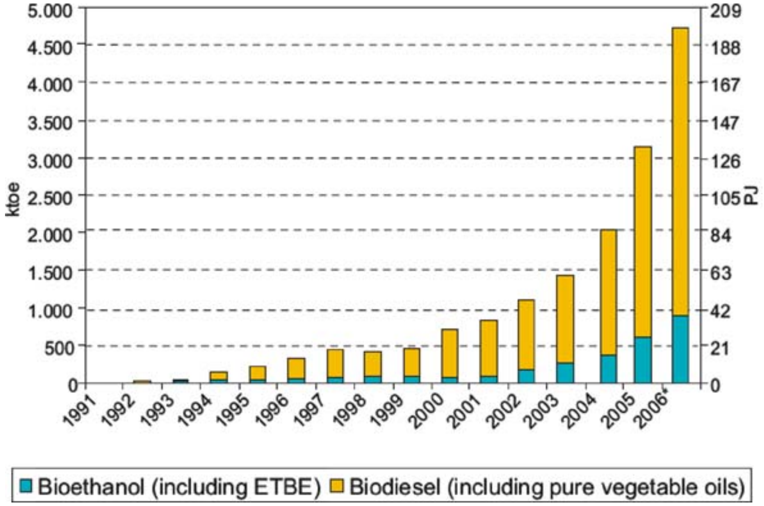

Fig. 8.1 Biofuels consumption (1991–2006) in the EU27
Source: REFUEL, IEA, Eurovserv' ER. Reproduced with permission of Marc Londo.

Ideally, such oil alternatives should reduce (or even remove) the dependence of oil as well as contributing as much as possible to meet the GHG emissions target. However, it is also widely accepted that joint efforts from politics, regulators, scientists and consumers will be needed to support an independent oil/GHG controlled scenario in the future.

On the view of the predictions, the need for a secure energy supply for transportation make essential to explore biofuels as alternative to mineral oil based fuels addressing and evaluating socio-economic and environmental consequences originated in their implementation.

From a wider context, there are three main drivers for the promotion, development and implementation of biofuels in our society. In principle, these are energy independence, climate change and rural development [3]. The political motivation to support biofuels arises from each individual driver or combinations of them. The main theoretical reasons for the promotion of biofuels can be summarised as follows:

1. *Biofuels can improve independence and energy security*. Local, national or global production of energy can avoid the reliance on politically and/or socially unstable energy suppliers [7]. In addition, the global oil demand is increasing exponentially and there is a need to find alternatives to fossil fuels derived from petroleum.
2. *Biofuels may contribute to a reduction in carbon emissions (aka climate change mitigation).* They have been often considered a solution to climate change. In fact, net emissions from biofuels have been reported to be remarkably lower than those generated from the combustion of fossil fuels [8, 9]. Nevertheless, the GHG emissions from the production of biofuels are a key issue that needs careful attention as they arise from every single stage in the supply chain from feedstock production and transport to conversion, biofuels distribution and end use (Fig. 8.2). Recently, some studies point out the CO_2 reduction may be far less than originally thought due to the inclusion of crop production costs including fertilisers, machinery, etc. as well as harvesting, transformations and distribution [3].
3. *Biofuels can help to increase farm income and contribute to rural development.* With a growing biofuels market, many countries will be able to grow more type of crops to cover national or foreign demands on energy crops. The increasing demand for agriculture due to the labour-intensive plant derived technologies [10] is expected to improve farm income, which in countries with oversupply can also help to reduce the need for subsidies. Traditionally deprived rural areas could experience a renaissance through the implementation of biofuels and biorefineries. In addition, there is also a lot of controversy over food vs fuel and the growth of specific crops to be transformed into biofuels. The resolution of this process will necessarily take place on the basis of very different variables over time [11].

With a wide array of potentially renewable energy resources, the concept and proposed benefits evolving from the use of biofuels are inspiring; therefore they

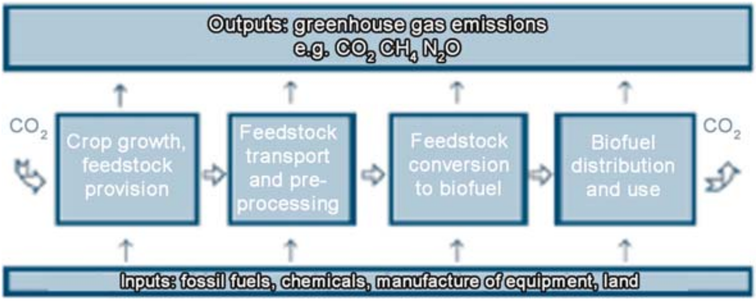
Outputs: greenhouse gas emissions
e.g. CO2, CH4, N2O
CO2
Crop growth, feedstock provision
Feedstock transport and pre-processing
Feedstock conversion to biofuel
Biofuel distribution and use
CO2
Inputs: fossil fuels, chemicals, manufacture of equipment, land

Fig. 8.2 Greenhouse gas emissions from production and utilisation of biofuels
Source: Sustainable biofuels: prospects and challenges, The Royal Society. Policy document 01/08, ISBN 978 0 85403 662 2. Reproduced with permission of the Royal Society.

need to be taken into account in order to contribute to a sustainable and energy secure future.

In this contribution, we aim to provide a general overview of the state of the art in the production and potential of biofuels for transport. Several technologies have been disclosed for the preparation on biofuels. Depending on the technology and the feedstock, we can classify the biofuels into different generations from simpler and conventional technologies and feedstocks (1st generation) to more advanced technologies (2nd generation and a potential 3rd generation in the horizon) in the so-called *biofuels ladder*.

8.2 Biofuels: Processes and Technologies

8.2.1 First Generation Biofuels

The first generation biofuels referred to biofuels manufactured from readily available energy crops including sugar, starch and oil crops (*edible feedstocks*) using conventional technologies. The most common first generation biofuels are biodiesel and bioethanol. Some other biofuels in this category including biofuels integrating glycerol, biofuels from catalytic cracking and biobutanol will also be briefly discussed. The various biofuels will be grouped according to the technology employed for their preparation. These are *chemical* and *biological* conversion.

8.2.1.1 Biofuels Produced by Chemical Conversion

Biodiesel

First generation biodiesel is currently the most common biofuel in Europe. It remains in the political and economic arena and is playing a part in the biofuels expanding process as the awareness alternative fuel spreads through the consciousness of the general public. Only in 2007, 19 biodiesel plants in the new EU member states were starting operations, or were under construction/planning. Relatively large plants can be found in Lithuania, Poland and Romania, with capacities of 100,000 tonnes/year. The conventional methodology for the production of biodiesel involves the transesterification of triglycerides (TG) from vegetable oils (palm, corn, soybean, rapeseed, sunflower, etc.) with short chain alcohols including methanol and ethanol to yield fatty acid (m)ethyl esters (FAM/EE) and glycerol as by product (Figs. 8.3 and 8.4).

Several reviews on the preparation of biodiesel from different feedstocks can be found in the literature [12–15]. A very good overview of such technologies has been

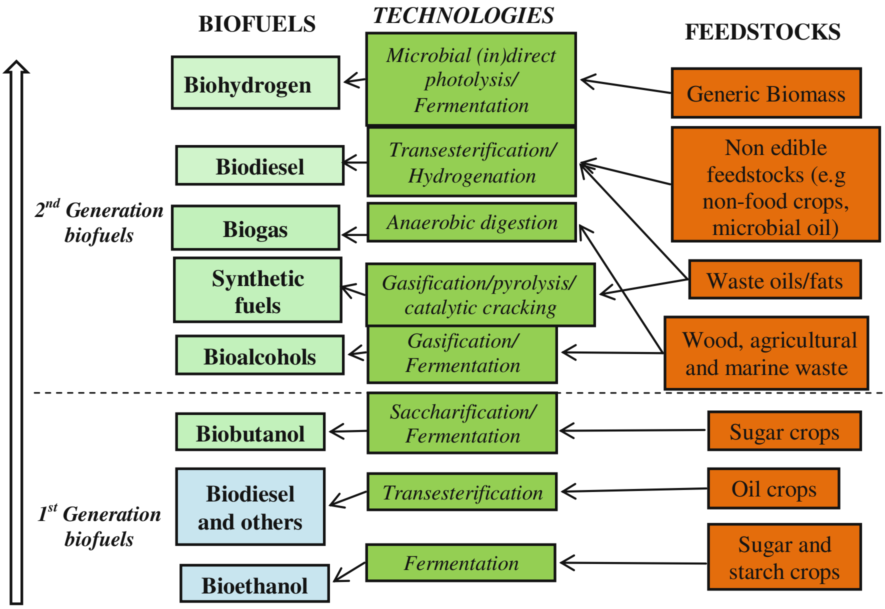

Fig. 8.3 The biofuels ladder. Road map of biofuels production from feedstocks and technologies

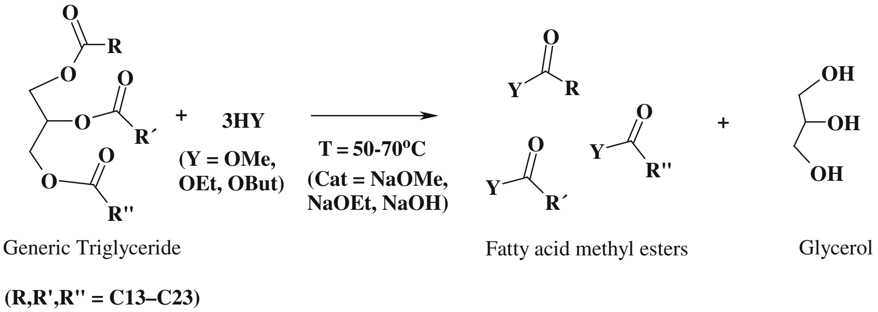

Fig. 8.4 Conventional transesterification of TG for the production of biodiesel

recently published by Al-Zuhair [16]. The methods of preparation of biodiesel can be classified in: chemical catalytic (base- or acid catalysis), biocatalytic (enzyme catalysis) and non-catalytic processes.

Biodiesel Produced by Chemical Catalytic Methods

a. Homogeneous catalysis. The conventional and traditional methodology for the production of biodiesel primarily involved the transesterification of the vegetable oils using NaOH and KOH [17–21] or mineral Brönsted acids (sulphuric, phosphoric or hydrochloric acids) [22–24] as homogeneous catalysts and vegetable oils or waste oils and fats as feedstock at relatively mild temperatures (50–80°C). Few reports on the production of biodiesel using a variety of homogeneous catalysts including guanidines [25] and different amines as catalysts (yielding conversions higher than 98% in a one-step reaction, minimizing the production of waste water) [26] can also be found.

Regardless of the limitations of the methodology, the process is also far from being environmentally friendly. The final mixture needs to be separated, neutralised and thoroughly washed, generating a great amount of salt, soaps, and waste water which need to be further purified or treated. The catalyst cannot also be recycled. These several additional steps certainly put the total overall biodiesel production costs up, reducing at the same time the quality of its main by-product (glycerol). This phase needs to be separated from the biodiesel for further washing/drying to remove the traces of glycerol aand from the fuel to comply with EU quality standard regulations (EN 14214). The standard prescribes 0.02% or lower glycerol content must be present in the biodiesel.

The acid catalysed homogeneous transesterification has not been widely investigated compared to the alkali-catalysed process due to its slower reaction rates, the need of harsher conditions (higher temperatures, methanol to oil molar ratios and quantities of catalysts) and the formation of unwanted secondary products such as dialkyl or glycerol ethers [15]. These drawbacks make impractical its successful implementation with hardly any examples of commercial processes available [27].

b. Heterogeneous catalysis. Several reports can be recently found on the production of biodiesel involving other chemically catalysed protocols as greener alternatives using vegetable oils using solid bases [28–32] and solid acids [24, 28, 33–37]. Di Serio et al. have recently reviewed the use of heterogeneous catalysts for biodiesel production [28]. The advantages of the heterogeneously catalysed protocols from the green chemistry standpoint are that the catalyst may be recycled and subsequently employed in the reaction. The biodiesel prepared has improved properties compared to the homogeneously catalysed process. The elimination of the pre-treatment steps and the minimisation of waste, avoiding the production of waste salts, also improves the green credentials of the reaction. Excellent yields of FAME/FAEE can be obtained under relatively mild conditions with many of these heterogeneous catalysts. However, the separation, disposal or use of the glycerol generated in the process as well as the washing of the crude biodiesel obtained to remove the traces of glycerol to meet the EEC regulations are often a problem associated to the chemical production of biodiesel.

Biodiesel Produced by Biochemical Catalytic Methods

The increasing environmental concerns have led to a growing interest in the use of enzyme catalysis as it usually produces a cleaner biodiesel under milder conditions. It also generates less waste than the conventional chemical process. Many authors have reported a wide range of efficient and low energy intentive protocols obtaining very promising results with lipases (in both free and immobilised form) [38–43] and combining lipases with alkali catalysts [44].

The limitations of the industrial use of enzymatic methodology is mainly due to their high production costs, which may be overcome by molecular technologies to enable the production of the enzymes in higher quantities as well as in a virtually purified form [45, 46].

Biodiesel Produced by Non-catalysed Processes

The most common and simple non-catalysed biodiesel production process has been performed using supercritical methanol via simultaneous transesterification of triglycerides and esterification of fatty acids [47, 48]. The supercritical alcohol conditions are essential because a very low reaction rate is obtained under subcritical conditions.

The procedure has been claimed to be very effective yielding high FAME contents in a very short time of reaction (typically less than 30 min). The presence of water also facilitated the formation of the methyl esters. Nevertheless, the supercritical methodology is still very expensive and the implementation of such costly technology in industry is currently a challenge.

8.2.1.2 Biofuels Produced by Biological Conversion

Bioalcohols

Bioethanol

Bioethanol is the other common first generation biofuel that is generally used as a blend that can go up to 85% content (E85) [49]. It is the most employed biofuel on a world level with the US currently being the world's largest producer and Brazil the largest exporter, accounting together for 70% of the world's production and 90% of ethanol used for fuel [49]. In Sweden and the US, a high-proportion bioethanol blend E85 (85% ethanol and 15% petrol) is being used in Flexible Fuel Vehicles (FFVs) with modified engines that are able to run on either E85 or petrol, or any mixture of the two.The E85 can nowadays be also purchased in several petrol stations in the UK (Fig. 8.5). Neat ethanol (E100) has also been employed in large scale in Brazil in specially modified engines.

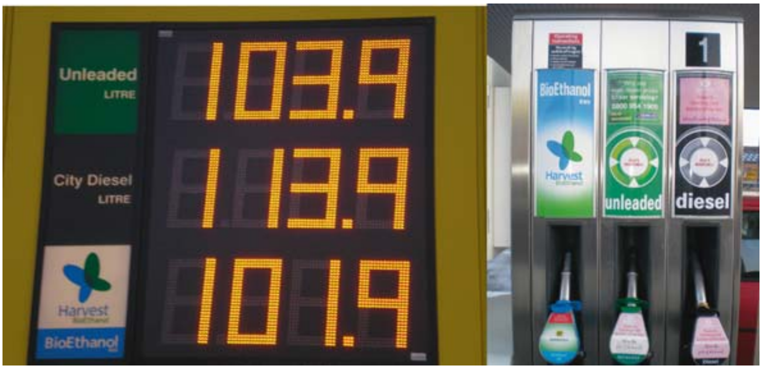

Fig. 8.5 E85 bioethanol blend can be found at cost-competitive prices in many petrol stations all over the UK (May 2008)

The common feedstocks employed for the production of first generation bioethanol are energy crops including sugar cane, corn, wheat, maize and sugar beet ("food" crops) although a great potential of grain or sweet sorghums in replacing maize and sugar cane, respectively, has been reported [50].

First generation bioethanol is generally obtained by biological conversion involving two key steps: hydrolysis and fermentation, followed by a distillation and dehydration of the bioethanol produced to obtain a higher concentration of alcohol to make it suitable for its use as automotive fuel.

Hydrolysis (saccharification). The digestion of the feedstock is normally performed via enzymatic hydrolysis using mixtures of amylases enzymes to convert the starch into sugars. Sugar cane and beet directly produce sugars that can be directly fed into the bioreactor.

Fermentation. The released sugars are subsequently fermentated to ethanol using yeast (e.g. *Saccharomyces cerevisiae*) using a similar process to that used in beer and wine-making [51, 52]. The invertase enzymes present in the yeast catalyse the conversion of sucrose into glucose and fructose that are subsequent transformed into ethanol and carbon dioxide by the zymases enzymes (Fig. 8.6).

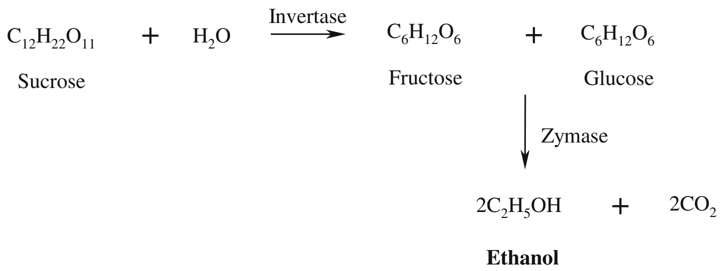

Fig. 8.6 Production of bioethanol via fermentation of hydrolysed sugars from energy crops

Bacteria strains such as *Zymmomonas mobilis* have been demonstrated as an alternative to yeats offering several advantages in the fermentation including higher specific productivity, ethanol yield and alcohol tolerance [3].

Biobutanol

Biobutanol (also denoted as biogasoline) is another interesting candidate that recently entered the battle of the alcohols and has the potential to become one of the key biofuels of the future due to its interesting properties [53–56].

The biobutanol is produced via fermentation in which the sugars from the source (so far from edible feedstocks) are firstly converted to butyrate and hydrogen, then turned into butanol via fermentation using various bacteria strains [53, 54]. The process has been reported to work with a wide range of bacteria and biomass [53–57]. Four main species have been in use, namely *C. acetobutylicum*, *C. beijerinckii*, *C. saccharoperbutylacetonicum* and *C. saccharobutylicum*. Most data are available from *C. acetobutylicum* that has been widely employed in the fermentation of starchy raw materials [53, 54].

Dupont and BP announced a partnership in 2006 to develop the next generation of biofuels, with biobutanol as first product [56, 58, 59]. A biobutanol demonstration plant has recently started to be built at an existing BP site in the UK that is expected to start test production of biobutanol by 2009 using sugar beet as feedstock [58, 59]. Similar biobutanol pilot plant projects are also ongoing in the US [60].

8.2.2 Second Generation Biofuels

Alternative feedstocks, generally *non-edible feedstocks* including waste vegetable oils and fats, non-food crops and biomass sources, and/or technologies were implemented/developed in an attempt to overcome the major shortcomings of the production of first generation biofuels. The biofuels obtained from such technologies have been denoted as second generation biofuels [61]. In theory, these can solve these problems and can supply a larger proportion of fuel supply in a more sustainable and reasonably priced way with greater environmental benefits (Fig. 8.7).

Several advances have been made in the last few years/months. The majority of the second generation biofuels processing technologies are not yet available on a fully commercial scale so the biofuels are expected to enter the market within a few years. Moreover, the development of many other approaches are currently ongoing and many more are to be reported, so the list included below, far from being exhaustive, provides the most interesting technologies reported until very recently. Second generation biofuels will be classified in various groups depending on the technologies employed for their preparation. In a similar way to those of the first generation biofuels, these are prepared by *chemical, thermo-chemical and biological* conversion.

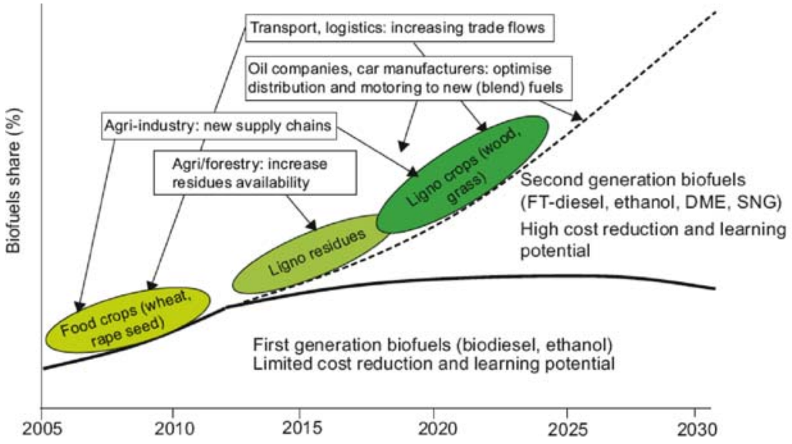

Fig. 8.7 Road map of potential development pathways for first and second generation biofuels, including implications for different markets
Source: REFUEL. http://www.refuel.eu/fileadmin/refuel/user/docs/REFUEL_final_road_map.pdf. Reproduced with permission of Marc Londo.

8.2.2.1 Biofuels Prepared by Chemical Conversion

Biodiesel from Non-edible Feedstocks (Via Transesterification)

Biodiesel from Non-food Crops

A second type of feedstock becoming relevant for the production of biodiesel is the so-called non-edible raw materials including non-food crops and waste oils and fats. Non-food crops, generally not suitable for human consumption or animal feed, have comparable or even higher oil yields (27–40% w/w) and lower resource consumption (i.e. cultivation inputs) than conventional ‘food’ crops [62], making then specially suitable for a more sustainable biodiesel production, in terms of a more efficient use of resources, minimal interaction with food crops and expected lower environmental impact [63].

Examples of these crops including *Brassica carinata* [64–67] and *Jatropha curcas* [63, 66–68] for the preparation of biodiesel have recently been reported. *Jatropha* is a particularly good example of a non-food crop for biofuel production since it thrives on poor soil and land unsuitable for food crops, actually creating topsoil, and gives a high oil yield.

The preparation of biodiesel from non-food crops is very similar to the chemical transformations (transesterifications) previously described for the use of traditional vegetable oils from food crops. Brazil opened in summer 2007 its first commercial Jatropha biodiesel facility (Compahnhia Productora de Biodiesel de Tocantins) with an estimated production of 40,000 tonnes biodiesel/year by the end of 2008 [69]. Some other *Brassica* and *Jatropha* projects including pilot plants in India, Africa and South America are also ongoing.

Biodiesel from Used Vegetable Oils (UVO) and Fats

UVO and animal fats are also considered as very attractive feedstocks for the production of biodiesel due to their lower market value compared to virgin oils and the fact of being recycled materials from other industrial sectors [70, 71]. The processing of the oil often requires a reduction of the high content FFA via acid catalysed esterification before the actual raw material can be transesterified to biodiesel [50].

Kulkarni et al. have recently reported the use of a heterogeneous solid acid catalyst that is able to carry out a simultaneous esterification of the free fatty acids and transesterification of the triglycerides, giving high FAME yields [72]. Efficient and low energy intentive protocols of the production of biodiesel from waste oils and animal fats combining lipases with alkali catalysts have also been reported [73].

Biodiesel from Microbial Oil (Via Transesterification)

Biodiesel from algae oil. Research is currently ongoing into the production of biodiesel from microalgae, which are believe to afford greater oil yields than any known feedstock as has been recently reported [74, 75].

Microalgae are sunlight-driven cell organisms that convert atmospheric CO_2 (via photosynthesis) into a plethora of chemicals including methane, hydrogen, polysaccharides and oil [74–76]. The production of microalgal oil is remarkably more efficient compared to conventional oil crops, providing higher oil yields (up to a 75% dry weight) and lower land area utilisation (Tables 8.1 and 8.2).

The process involves the extraction of the oil from microalgae and subsequent transesterification with alcohols using homogeneous or heterogeneous catalysts (in a similar way to that of biodiesel obtained from (non) edible feedstocks) to give biodiesel.

Significant advances in the field have been recently reported with biodiesel from microbial oil. Cellana, a joint venture of Shell and HR Biopetroleum recently started the construction of a pilot facility in the Kona coast of Hawaii Island to grow algae as biofuel feedstock [77].

Biodiesel from other microbial oils. Many reports can be found on the subject using different microbes including various yeast and bacteria [78–80]. A summary of the main reported microorganisms and their respective oil yields have been included in Table 8.3.

Table 8.1 Microbial oil content (% dry weight) of various algae species [74, 75]

Microalgae	Oil content (% dry wt)
Botryococcus braunii	25–75
Chlorella sp.	28–32
Cylindrotheca sp.	16–37
Nannochloropsis	31–68
Nitzschia sp.	45–47
Schizochytrium sp.	50–77

Table 8.2 Comparison of oil yield vs required land for different biodiesel feedstocks in the US [74, 75]

Crop	Oil yield (L/ha)	Required land (M ha)[a]
Microalgae[b]	136,900	2
Microalgae[c]	58,700	4.5
Oil palm	5950	45
Jatropha	1,892	140
Canola	1190	223
Soybean	446	594
Corn	172	1540

[a] To meet 50% of all US current transport consumption;
[b] 70% (w/w) oil yield in biomass;
[c] 30% (w/w) oil yield in biomass.

Table 8.3 Oil production (oil content and yield) of different microorganisms grown on various carbon sources [79, 80]

Microorganism	Carbon source	Biomass (g/L)	Oil content (%)	Oil yield (g/L)	References
Trichosporon fermentans	Molasses	36.4	35.3	12.8	[78]
Lipomyces starkeyi	Sewage sludge	9.4	68.0	6.4	[79]
Mortierella isabellina	Starch	10.4	36.0	3.7	[80]
	Pectin	8.4	24.0	2.0	
Cunningamella echinilata	Starch	13.5	28.0	3.8	
	Pectin	4.1	10.0	0.4	

In general, the cultivation of such microorganisms is not dependent on seasons or climate. They can also be easily grown on a variety of inexpensive substrates including waste residues from agriculture and industry [79], providing they have the nutrients needed for the microorganisms.

8.2.2.2 Biofuels Produced by Thermo-(Chemical) Conversion

Biofuels included under this headline are also prepared from various non-edible biomass feedstocks. Thermo-chemical conversion pathways include processes such as gasification and pyrolysis (Fig. 8.8) [81–83].

Biofuels from Gasification

The process involves the partial combustion of the feedstock to produce syngas (a mixture of carbon monoxide (CO) and hydrogen (H_2) denoted as bio-Synthetic Natural Gas, bio-SNG) via conventional or alternative gasification processes. Then, bio-SNG is subsequently transformed into liquid hydrocarbons (mostly diesel and kerosene-type fuels) and/or gases via different processes, leading to a variety of biofuels that will be outlined. Such prospective liquid/gas biofuels for transport

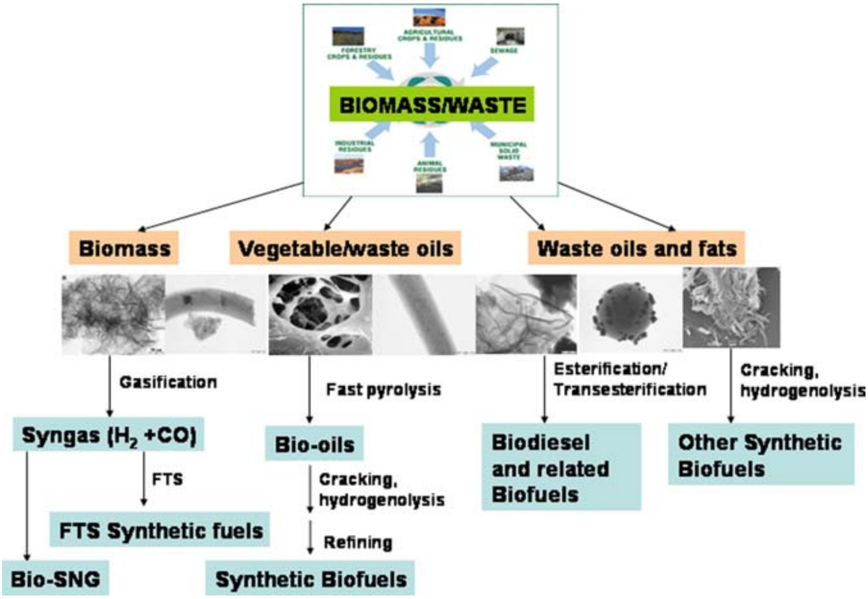

Fig. 8.8 Biomass gasification and pyrolysis routes to synthetic biofuels
Source: Sustainable biofuels: prospects and challenges, RS Policy document 01/08, ISBN 978 0 85403 662 2. Reproduced with permission of the Royal Society.

(Fig. 8.8) include bioalcohols (methanol, ethanol and linear higher chain alcohol mixtures) and synthetic biofuels.

At this point is worth mentioning that although bio-SNG could be classified as *synthetic biofuel,* it comes first since all the reported biofuels from gasification are obtained from it and thus the technologies (up to the preparation of the syngas) are very similar.

Bio-SNG

Bio-SNG can be produced by a conventional gasification process (methanation) at high temperatures (800–1000°C) aiming at producing large quantities of methane. The current technology employed allows the use of a wide range of biomass feedstocks including wood chips and waste wood [84–86]. The conventional gasification process involves various steps (Fig. 8.9). Firstly, the biomass undergoes endothermal steam gasification (reaction 1) to give a mixture of CO and H_2, which is subsequently converted into methane, CO_2 and hydrogen (reactions 2 and 3). The net overall reaction from biomass to methane and CO_2 (reaction 4) is slightly exothermic. However, the main drawback of the conventional gasification technology is the formation of tars and char [87].

Interestingly, the gasification of biomass can be performed at lower temperatures (250–400°C) in supercritical water. It has currently been reported at lab scale, employing different Ni and Co based catalysts [86]. In this process, the biomass

$$(1)\quad CH_{1.49}O_{0.67}(s) + 0.33\,H_2O(g) \longrightarrow CO + 1.08\,H_2$$

$$(2)\quad 0.52\,CO + 1.56\,H_2 \longrightarrow 0.52\,CH_4 + 0.52\,H_2O(g)$$

$$(3)\quad 0.48\,CO + 0.48\,H_2O(g) \longrightarrow 0.48\,CO_2 + 0.48\,H_2$$

$$(4)\quad CH_{1.49}O_{0.67}(s) + 0.29\,H_2O(g) \longrightarrow 0.52\,CH_4 + 0.48\,CO_2$$

Fig. 8.9 Reactions involved in the conventional gasification of biomass

disintegrates in supercritical water forming a mixture of carbon dioxide, carbon monoxide and methane (SNG). The technology is expected to be especially suitable for wet (polluted) biomass and has higher efficiency than the conventional gasification process at lower temperature [86]. Bio-SNG can also be produced from biogas.

Various projects in the Netherlands, including the largest existing bio-SNG plant located in Buggenum, currently produce bio-SNG from the co-gasification of biomass with coal at different proportions [88].

Bioalcohols

Biomethanol. Biomethanol can be produced from synthesis gas [89] via conventional gasification of biomass (partial oxidation) at high temperatures (800–1000°C) and subsequent catalytic synthesis of the $CO+H_2$-in a 1:2 ratio-under high pressures (4–10 MPa) [89–91].

The biofuel can be blended with petrol up to 10–20% without the need of any engine modifications [90, 91]. Several feedstocks including bark, woodchips, bamboo, waste wood and pulp [89–91] and even glycerol [92] have been reported to be used in the process.

There are a few biomethanol pilot plants under development, mainly in the US (e.g. North Shore Energy Technologies, 40 MMgy plant) and Japan (e.g. Norin Green no1, MAFF and Mitsubishi heavy industries) [90].

Bioethanol. Bioethanol can be also obtained via conventional thermal gasification of biomass to syngas combined with catalytic processes in similar way to those for the production of biomethanol (Fig. 8.11, left side) [3].

Alternatively, following biomass gasification, the syngas can be directly fermented to ethanol using anaerobic bacteria (Fig. 8.11) [93]. This eliminates the need of the hydrolysis step to break up the cellulose and hemicellulose fractions of the biomass. The lignin fraction can also be converted into ethanol. The process has been reported at lab scale and is still under development [3, 93]. However, the efficient delivery of the syngas to the microorganisms still remains a challenge [3].

There are some examples of ongoing industrial processes. An operating lignocellulosic bioethanol production plant is located in Ottawa (Canada), run by the IOGEN Corporation [94]. The demonstration plant produces up to 3 million litres of bioethanol per year. The feedstocks employed are wheat, oat and barley straw. A bioethanol plant in Ulmea (Sweden) is running using waste stream of cellulose-based materials and another pilot plant production for the preparation of bioethanol from lignocellulosic materials (e.g. Norway Spruce) has recently started production [95].

Linear bioalcohol mixtures. Mixed linear alcohols (i.e., mixtures of mostly ethanol, propanol and butanol, with some pentanol, hexanol, heptanol and octanol) can also be produced from syngas in a similar way to that described for methanol and ethanol [96]. One of such linear alcohol mixtures denoted as Ecalene^{TM} is currently registered with the US Environmental Protection Agency per 40 CFR 79.23 as a fuel blending additive [96].

Synthetic Biofuels

Synthetic biofuels can be defined as fuels prepared from syngas via different processes. Bridgwater and Demirbas have recently reported comprehensive overviews of the development of these technologies for the preparation of biofuels [87, 89].

Under this headline we can include a selection of some interesting options such as biofuels obtained by steam reforming, HydroThermalUpgrading (HTU) and Fischer-Tropsch Synthesis (FTS).

Biofuels obtained by steam reforming. Steam reforming can be applied to various solid waste materials including organic waste, sewage sludge, waste oils, black liquor and agricultural waste to produce biofuels [89]. Steam reforming of natural gas (often referred as steam CH_4 reforming) is the most common method to produce commercial H_2 [89].

Biohydrogen can therefore be produced from a biomass feedstock via conventional gasification at high temperatures to syngas to obtain methane (reaction 4, Fig. 8.9) and subsequent steam CH_4 reforming at high temperatures (700–1100°C) using Ni supported catalysts (e.g. Ni/Al_2O_3, Ni/MgO) at 3–25 bar pressure (Fig. 8.10, reaction 1) [89, 97]. For the production of high purity H_2, the reforming of the biofuel that includes multiple catalytic steps is followed by two water gas-shift (WGS) reaction steps (Fig. 8.10, reaction 2), a final CO purification and removal of the remaining CO_2 by pressure swing adsorption or ceramic membrane separation [89, 97].

Alternatively, the gasification step of biohydrogen can also be performed in supercritical water (in a similar way to that of the bio-SNG) with the advantages of the direct use of wet biomass without drying and a high gasification efficiency at lower temperature [89, 98]. However, the cost of H_2 production using this technology is several times higher than the current price of H_2 obtained from steam reforming [89].

$$(1)\quad CH_4 + H_2O \longrightarrow CO + 3H_2$$

$$(2)\quad CO + H_2O \longrightarrow CO_2 + H_2$$

Fig. 8.10 Steam CH_4 reforming (1) and WGS (2) reactions for the preparation of biohydrogen

Biofuels obtained via HydroThermal Upgrading (HTU). HTU-diesel can be produced from various feedstocks including dry (wood and lignocellulose) [99] and wet (beet pulp, sludge or bagasse) biomass [100–102]. The methodology involves the hydrothermal treatment of biomass that is converted into a mixture of hydrocarbons at relatively low temperatures (250–350°C) and moderate (autogenous pressure) [99] to high (120–180 bar) pressures [100, 101].

The biocrude obtained is a heavy organic liquid immiscible with water that contains a wide range of hydrocarbons including acids (e.g. acetic acid), alcohols (e.g. isopropyl alcohol) and phenolic derivatives (in the particular case of lignocellulosic materials) [99–102]. Often, the hydrocarbon mixture obtained needs further processing [via catalytic hydro-de-oxygenation (HDO)] to yields a liquid biofuel similar to fossil diesel that can be blended with fossil diesel in any proportion without the necessity of engine or infrastructure modifications [102]. HTU research has been mainly performed in The Netherlands, with an HTU demonstration plan in Amsterdam that is able to generate over 12,000 tonnes of biocrude (including ash) per year [100, 101].

Biofuels obtained via Fischer-Tropsch Synthesis (FTS). The Fischer-Tropsch (FT) process is one of the advanced biofuels conversion technologies. It has been known since 1923 when German scientists Franz Fisher and Hans Tropsch aimed to synthesize long-chain hydrocarbons from a CO and H_2 gas mixture, but it was mainly used in the past for the production of liquid fuels from coal or natural gas [103, 104].

Prior to the FTS, the gasification of biomass feedstocks takes place in a similar way that described for the production of bio-SNG (Fig. 8.9). Then, a cleaning and conditioning step of the produced syngas is normally performed to remove all the impurities present prior to the catalytic reaction to minimise the poisoning of the catalyst [105, 106].

The FTS process is then carried out. It comprises of various steps described by the set of equations in Fig. 8.11, where x is the average length of the hydrocarbon chain and y is the number of H_2 atoms per carbon.

The first step involves the reaction of CO with H_2 in the presence of a Co or Fe catalyst (Fig. 8.10, top reaction) to afford a hydrocarbon chain extension ($-CH_2-$) that is a building block for the formation of longer hydrocarbons. Typical operation conditions are temperatures between 200 and 400°C and 15–40 bar pressures, depending on the process [89, 103, 104].

All reactions are exothermic and the product is a sulphur free mixture of different predominantly linear hydrocarbons (primarily alkanes and alkenes) that frequently undergoes upgrade and refining steps to be turned into automotive fuels, namely FT-diesel (main product) and gasoline-like biofuels (by-products) [89]. The FT

$$x\mathrm{CO} + 2x\mathrm{H_2} \longrightarrow (\text{-}\mathrm{CH_2}\text{-}) + x\mathrm{H_2O}$$

$$x\mathrm{CO} + 2(x{+}1)\mathrm{H_2} \longrightarrow \mathrm{C_xH_{2x+1}} + x\mathrm{H_2O}$$

$$x\mathrm{CO} + (x + y/2)\mathrm{H_2} \longrightarrow \mathrm{C_xH_y} + x\mathrm{H_2O}$$

Fig. 8.11 FTS reactions for the production of linear long-chain hydrocarbons

catalysts are mainly based on iron and cobalt [89, 103, 104, 107, 108]. Cobalt catalysts have the advantage of a higher conversion rate and they are also more reactive in hydrogenation, producing less unsaturated hydrocarbons and alcohols compared to iron catalysts that produce higher alkenes and oxygenates content [89, 103, 104].

The process using biomass as feedstock is currently under development. In theory, there are no restrictions in the type of biomass that can be used as feedstock. Woody and grassy materials and agricultural and forestry residues have been investigated in the process [107–109].

Pilot production facilities for Fischer-Tropsch liquids from biomass are currently in operation in Germany (e.g. Lurgi and Choren) and the Netherlands [88].

8.2.2.3 Biofuels Produced by Biological Conversion

Bioalcohols

Bioethanol. Second generation bioethanol is usually produced from a range of alternative readily abundant and inexpensive cellulosic biomass feedstocks including woody biomass, grasses, forestry and agricultural waste [110, 111]. Very interesting reviews about the progress in bioethanol and lignocellulosic processing have been recently reported [51, 112, 113].

An overview of the production routes of second generation bioethanol is included in Fig. 8.12.

The process (Fig. 8.12, right hand side) is identical to that described in the production of first generation bioethanol: decomposition of the material into fermentable sugars (hydrolysis) and transformation of the sugars into bioethanol (fermentation).

The main changes are the processing technologies and the feedstocks that usually account for the majority of the plant cost. Cellulosic biomass comprises of two main components. Cellulose and hemicellulose (complex carbohydrate polymers), accounting roughly for about a 70–75 wt% of the lignocellulose. A mixture of enzymes (cellulases and hemicellases) different from those of the first generation bioethanol production are employed in the hydrolysis step. In the particular case of lignocellulosic (woody) materials, lignin is obtained as by-product of the process. Lignin can be burned to produce heat and power for the processing plant and potentially for surrounding homes and businesses and it is to be hoped that

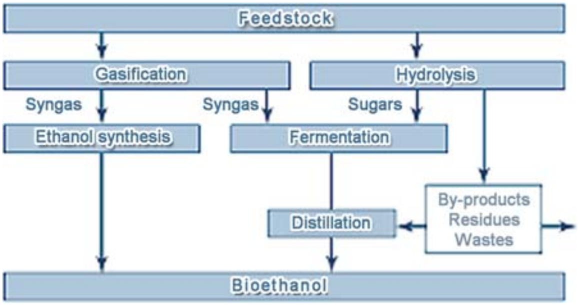

Fig. 8.12 Thermochemical and biological routes to second generation bioethanol Source: Sustainable biofuels: prospects and challenges, RS Policy document 01/08, ISBN 978 0 85403 662 2. Reproduced with permission of the Royal Society.

it can become a future source of aromatic chemicals and materials. Alternative organisms need also to be employed due to the impossibility of the traditional yeast and bacteria to process the pentose (C5) sugars derived from hemicellulose [114].

Branched alcohol mixtures. The preparation of a branched-longer chain alcohol mixture with a potential use as biofuel has been recently reported by Liao et al. [115]. Such alcohol mixture with high isobutanol content is produced via synthetic non-fermentative pathway employing metabolic engineered bacteria (e.g. *E. coli*) and glucose as carbon source. This strategy diverts the 2-ketoacid intermediates in the aminoacid biosynthetic pathway of *E. coli* for alcohol synthesis, converting them into aldehydes (by 2-ketoacid decarboxylases) and then to alcohols (by alcohol dehydrogenases) [115]. The process has been already licensed to Gevo (spin-off company from Pasadena, US) that hopes to begin commercial scale production within a few years [116, 117].

Biogas

Biogas is an environment friendly, clean, cheap and versatile fuel, composed of a mixture of CH_4 and CO_2 that is usually generated from bacterial digestion of biomass in absence of air between 10 and 72°C [83, 118]. Almost any type of organic matter (e.g. sewage sludge, animal wastes, industrial effluents) is suitable for the production of biogas, which can be directly utilised in cooking and heating systems [119]. The process is carried out in anaerobic digesters that can vary in size from 1 m^3 (small household unit) to as large as 2000 m^3 [120], involving a step-wise series of reactions that require the cooperative action of several microorganisms. Initially, a group of microorganisms (acidogens) break down the organic matter into a digestible form (usually simpler fatty acids) that can be utilised by methane-generating anaerobic bacteria (methanogens) that produce biogas as metabolic byproduct [121, 122].

The use of biogas as transport fuel has been explored in its application in explosion engines. Biogas has shown a great potential for its uses in Brazil [123] and in places such as Sweden, has been use in urban buses since 2004 [124]. Also in Sweden some studies have evaluated the economic and environmental feasibility of biogas as a renewable source of energy in large scale showing positive results in its applicability CHP (centralised heat and power) [125].

Biohydrogen

Various authors have recently reviewed the prospects and potential in the production of biohydrogen [126–130]. Biohydrogen can be produced by three different biological pathways: fermentation and direct or indirect (bio)photolysis.

Fermentation. Dark and photo fermentation are technologies under development (currently at lab scale) to produce biohydrogen from wet biomass (e.g. molasses, organic wastes, sewage sludge) using (an)aerobic hydrogen fermenting bacteria [130, 131]. The advantage of the dark fermentation is that the biohydrogen is produced directly without formation of methane [127, 130]. During dark fermentation, various organic acids are also produced. These compounds can subsequently be converted to hydrogen by a process denoted as photo fermentation.

Direct photolysis. In this approach, the process takes advantage of the photosynthetic capability of algae and cyanobacteria to split water into O_2 and H_2 via direct absorption of light and transfer of electrons to two groups of enzymes that participate in biological hydrogen metabolism: hydrogenases and nitrogenases [129].

Indirect photolysis. Alternatively, biohydrogen can be prepared through the use of some microorganisms (algae) that can directly produce hydrogen under certain conditions [126, 127, 129]. Most specifically, sealed cultures of green algae become anaerobic in the light under deprivation of sulfur nutrients and spontaneously induce the "hydrogenase pathway" to photosynthetically produce hydrogen [127]. Substantial rates of hydrogen production were obtained over 60 h in the light although the hydrogen production leveled off reaching a point (after 100 h) in which the algae go back to the normal photosynthetic pathway in order to restore the consumption of internal starch and proteins that takes place in the course of the hydrogen production [132].

8.3 Engine Performance of Biofuels

8.3.1 Diesel Engines Performance Using Biodiesel

Short- and long-term performance tests in diesel engines using biodiesel (mainly, ethyl and methyl esters from fats or vegetable oils including soybean, rapeseed and sunflower oils) have revealed an increase in the volumetric brake specific fuel consumption, due to the lower volumetric calorific value. Engine power and torque differ slightly or remain unchanged, while smoke emissions of biodiesel are much lower compared to diesel fuel [133–137]. Some of these properties of biodiesel compared to diesel fuel are summarised in Table 8.4.

To improve the combustion properties and cold-weather behavior, several investigations have recommended the use of biodiesel blended with diesel fuel in different percentages [139–142]. The heating value of biodiesel mixtures becomes higher than that of biodiesel due to the lower heating values and stoichiometric air/fuel ratios of biodiesel compared to diesel fuel [143]. A wide range of diesel engines of different sizes and types has been tested. Direct injection, turbocharged, and

Table 8.4 Fuel Specifications of biodiesel and mineral diesel fuel [138]

Property	Diesel fuel (EN-590)	Biodiesel (EN 14214)
Density at 15°C (kg/m^3)	820−860	860−900
Kinematic viscosity at 40°C (mm^2/s)	2−4.5	3.5−5
Flash point (°C)	> 55	> 120
Cetane number (CN)	> 46	> 51
Gross heating value, GHV (MJ/kg)	45−46	30−42

4-cylinder diesel engines have been the most frequently employed [144]. Since engine characteristics might have some influence on the effects of biodiesel, this information has to be taken into consideration.

8.3.1.1 Effect of Biodiesel on Engine Performance Properties

Brake effective power and power output. The power output delivered with biodiesel is reduced with respect to that delivered with diesel fuel at full- and partial-load conditions even with the accelerator fully pressed down. Although reductions around 8% (corresponding to loss of heating value) would be expected in most cases, results show some variations according to literature reports. Kaplan et al. [133] compared sunflower-oil biodiesel with diesel fuel at different engine speed and load regimes, in a 2.5 L, 53 kW engine. The loss of torque and power varied from 5% (at low speed) to 10% (at high speed). Çetinkaya et al. [136] compared waste-oil biodiesel with diesel fuel in a 75 kW 4-cylinder common rail engine under full-load conditions. The loss of torque was in the 3–5% range when biodiesel was used to replace diesel fuel. The authors pointed to the reduced heating value in biodiesel as the most plausible explanation for this reduction. Similar results were achieved by Lin et al. [142] in a naturally aspirated 2.84 L diesel engine running with diesel fuel, biodiesel from palm-oil and a 20% biodiesel blend. The loss of power at full load was around 3.5% with pure biodiesel and 1% with the blend. Similar results in terms of power loss have also been reported elsewhere [145, 146].

Some authors have claimed that there is a relationship between power losses and the reduction in heating value. Yücesu and Ilkiliç[147] measured reductions in torque and power of 3–8% when pure biodiesel from cottonseed was utilised. Interestingly, they also reported for biodiesel a heating value 5% inferior to that of diesel fuel. Difficulties in the fuel atomization (rather than the loss of heating value) was claimed to be the cause of the power loss. Other tests using biodiesel from waste cooking oil in a marine outboard 3-cylinder naturally aspirated engine at full load resulted in a power loss of 7.14% as compared with diesel fuel [148]. The difference in the biodiesel/diesel heating values was interestingly very close to this value. Dorado et al. [138] found a slight increase (5.7%) in the maximum engine power using waste olive oil methyl esters instead of diesel fuel. Only after the engine run on biodiesel for 50 h, a minor 2% loss in maximum power was observed.

There are also some publications reporting unexpected increases in engine power and torque when using biodiesel. Altiparmak et al. measured a 6.1% increase in maximum torque compared to diesel fuel when 70% tall-oil biodiesel blended with diesel fuel was used [149]. Although the increased cetane number was used to explain these findings, the unusually high values of density and viscosity of the tested biodiesel (922 kg/m^3 and 7.1 cSt at 40°C, respectively) could also partially explain such results. Similarly, an increase in torque and power was observed in an indirect injection diesel engine running at 1500 and 3000 rpm on different blends of diesel fuel with biodiesel from tobacco seed oil (with a lower heating value of 39.8 MJ/kg) [150]. The 17.5% biodiesel blend showed the highest values of torque, power, density, viscosity and improved combustion, despite the reduced heating value of biodiesel.

Various reasons have been reported to explain the torque and power recovery at full load (corresponding to the loss of heating value) of biodiesel with respect to diesel fuel.

The higher viscosity of biodiesel may affect the engine brake effective power, especially under full-load operating conditions. The increased injected volume has also been attributed to the increase in viscosity [150].

The higher bulk modulus and sound velocity of biodiesel, together with its higher viscosity, lead to an advanced start of injection [151]. This fact, together with an increase in the cetane number, may slightly advance the start of combustion. To reduce pressure and temperature peaks in the combustion chamber, and thereby nitric oxide formation, current diesel engines need to have delayed combustion. This delay involves a loss of thermal efficiency and consequently of brake effective power. If the start of injection, and thus that of combustion, is advanced, the combustion process is then re-centered and the power output increases [149, 152, 153].

The higher lubricity of biodiesel could also reduce the loss of friction leading to an increased brake effective power. Several researchers have used this argument to explain the increased thermal efficiency or power recovery in spite of the unknown origin of this improvement (reduction of mechanical losses in the injection pump and cylinder walls) [153]. In any case, it seems very unlikely that the lubricity can contribute to the torque and power recovery.

The concept of thermal barrier coatings may be useful to limit the effect of the high viscosity of biodiesel. Engines with thermal barrier coating are called low heat rejection (LHR) engine. The LHR concept is based on suppressing heat rejection to the coolant and recovering the energy in the form of useful work. Insulating the combustion chamber components of LHR engines can reduce heat transfer between in-cylinder gas and cylinder liner, thus enhancing engine power and torque due to the increased exhaust gas temperatures before the turbine inlet [143, 154].

Brake-specific fuel consumption (BSFC). BSFC is the ratio between mass fuel consumption and *Brake effective power*, being inversely proportional to the thermal efficiency. According to literature reports, the biodiesel specific fuel consumption is expected to increase around 10–20% in relation to diesel fuel, corresponding to the increase in heating value in mass basis. In other words, the loss of heating value of biodiesel has to be compensated with a higher fuel consumption. An indicator of the loss of heating value is the oxygen content in the fuel [144]. A correlation between BSFC and oxygen content has been found and the conclusions are the increase in BSFC is due to the oxygen enrichment from the fuel, but not from the intake air [155, 156].

Fuel consumption seems to behave proportionally to the loss of heating value, whether heavy-duty or light-duty engines were tested. Turrio-Baldassarri et al. tested a 6-cylinder 7.8 L engine with a 20% rapeseed-oil biodiesel (with a glycerin content of 1.15%)/diesel fuel blend [157]. They measured a BSFC increase of 2.95% with 95% statistical confidence. A similarly sized engine (6 cylinders and 170 kW of rated power) was tested by Hansen and Jensen with pure rapeseed-oil biodiesel measuring a 14% increase in BSFC [135].

Similar results have been reported considering a wider range of vehicle engine sizes. An increase of 2.5 and 14% in BSFC were obtained in a diesel engine running on 20% biodiesel/diesel fuel blend and pure biodiesel, respectively [158]. The performances of biodiesel from soybean and waste-oils compared in a 57 kW engine showed the feedstock did not have any influence on the BSFC [158]. Senatore et al. tested a 1.9 L diesel engine with rapeseed-oil biodiesel, and found that the increase in BSFC with biodiesel was proportionally related to the decrease of the lower heating value [159]. Similar results were reported for such biodiesel in a single-cylinder diesel engine tested in three steady modes [160].

Many research efforts have carried out in order to ascertain the implications of the properties of biodiesel in the BSFC. The increase in BSFC was reported to be similar to the loss of heating value in biodiesel from waste oils tested on a 2.2 L diesel engine [161]. Monyem and Van Gerpen tested a 4.5 L diesel engine with differently oxidized soybean-oil biodiesel [162]. The increase in BSFC was 13.8 and 15.1% for non-oxidized and oxidized biodiesel (peroxide index of 340 meq/kg). This difference was attributed to the different heating value of both fuels. Most authors have explained these increments by the loss of heating value, although some others attributed them to the different densities of biodiesel and diesel fuel [163]. Nevertheless, some reports moved away from these correlations and claimed no proportionality between the increase in BSFC and the loss of heating value. A 3.3 and 16.7% increase in BSFC (compared to the use of diesel fuel) were observed when using a 20% blend and pure palm-oil biodiesel, respectively [142]. Similarly, Hess et al. [164] found a 18% increase using pure biodiesel from soybean oil. In contrast to these findings, Silva et al. reported no significant changes in BSFC in a 6-cylinder 9.6 L diesel engine fueled with 5 and 30% sunflower-oil biodiesel/diesel fuel blends [146]. Similarly, Dorado et al. [138] evaluated the use of waste olive oil methyl esters during a 50-h short-term performance test in a 3-cylinder 2.5 L diesel engine and found a very slight BSFC increase. Nevertheless, the statistical analysis showed no important differences between biodiesel and No. 2 diesel fuel tests. Kaplan et al. also claimed that the fuel consumption decreased with biodiesel, causing a reduction in the emitted smoke and soot (smoke opacity) [133].

8.3.1.2 Diesel Engine Exhaust Emissions Using Biodiesel

Several approaches have found that, in general, biodiesel lead to less emissions (e.g. $CO_{2)}$ of the most regulated pollutants compared to standard diesel fuel. Biodiesel may then contribute to reduce greenhouse gas emissions [165–167]. Provided its oxygenated structure, biodiesel causes lesser particulate formation and exhaust emissions compared to diesel fuel, resulting in substantially lower unregulated emissions of carcinogenic compounds (i.e. ketones, benzene and aromatic compounds).

Smoke opacity is a direct measure of smoke and soot. Various studies show that smoke opacity for biodiesel is generally lower [133, 168, 169] with much lower emissions of hydrocarbons. This is also due to oxygenated nature of biodiesel where more oxygen is available for burning and reducing hydrocarbon emissions in the exhaust [169]. Nitrogen oxides (NO_x) can be very important in polluted air. Regionally high NO_2 concentrations can cause severe air quality deterioration. Practically all anthropogenic NO_x emissions enter the atmosphere as NO generated from the combustion of fossil fuels in internal combustion engines. Like carbon monoxide, NO binds to hemoglobin and reduces the oxygen transport efficiency. However, the concentration of NO normally is much lower than that of carbon monoxide so that the effect on hemoglobin is less significant [170]. In general, reported results have revealed an increase in NO_x emissions for biodiesel [137, 157, 171–173]. Dorado et al. tested a diesel direct injection Perkins engine fueled with waste olive oil methyl esters at several steady-state operating conditions. Results revealed that the use of biodiesel resulted in lower emissions of CO, CO_2, NO, and SO_2, with an increase in NO_2 emissions [138]. The efficiency of the combustion remained constant using both biodiesel and diesel fuel [137]. Recent reports pointed out the formation of higher quantities of NO_x can be correlated to the higher temperatures and quantities of oxygen expected in the combustion chamber due to the improved biodiesel combustion [174, 175]. However, the lower sulfur content present in biodiesel may allow the use of designer control technologies (e.g. catalysts) to the abatement of NO_x emissions that cannot be otherwise employed with conventional diesel.

The fact of the improved combustion process is partially believed to be a result of the advanced injection derived from the optimum physical properties of biodiesel (viscosity, density, compressibility, sound velocity) [175], in good agreement with a variety of reports [152, 153, 159]. Monyem and Van Gerpen [162] found a good correlation between the start of injection and NO_x, independently of the fuel used, which suggests this is the only reason for NO_x increase. Another plausible explanation points to the electronic improvements in the injection pump when biodiesel is used instead of diesel fuel [176]. Thus, it seems that the main reasons for the increase of NO_x emissions using biodiesel as fuel are injection-related.

The acid rain, caused by the deposition on the earth's surface of acids (e.g. SO_2), can be mostly attributed to industrial operations emissions and fossil fuel combustion. As a result of its widespread distribution and effects, it is an air pollutant that may pose a threat to the global atmosphere [170]. Nevertheless, since biodiesel is sulfur-free, less sulfate emissions and particulate reduction are reported in the exhaust and thus it may contribute to reduce the problem of acid rain due to transportation fuels [174].

8.3.2 Spark Ignition Engines Performance Using Bioethanol

Bioethanol is an oxygenated fuel containing 35% oxygen that exhibits a higher octane number (108), lower cetane number (less than 10), broader flammability limits, higher flame speeds and higher heats of vaporization than gasoline [51, 177]. These properties lead to a higher compression ratio, shorter burn time and leaner burn engine, enhancing the theoretical efficiency over gasoline [178]. The autoignition temperature and flash point of ethanol are higher than those of gasoline, which

Table 8.5 Some properties of ethanol, gasoline and diesel fuel [51, 180]

Property	Gasoline (EN 590)	Diesel fuel (EN 590)	Ethanol
Specific gravity (at 15°C)	0.73	0.82	0.79
Boiling point (°C)	30–225	190–280	78.3
Specific heat (MJ/kg)	43.5	43.0	27.0
Heat of vaporization (kJ/kg)	400	600	900
Octane number	91–100	–	108
Cetane number	Below 15	40–60	Below 15
Flashpoint (°C)	–40	64	13
Auto ignition temperature (°C)	300	230	366

makes it safer for transportation and storage. Some properties of ethanol, compared to diesel fuel and gasoline are showed in Table 8.5. However, bioethanol has several drawbacks including a 66% lower energy density compared to gasoline, corrosiveness, low flame luminosity, lower vapor pressure (making cold starts difficult) and its miscibility with water and relative toxicity to ecosystems [51, 179].

Due to its lower volatility and photochemical reactivity in the atmosphere compared to gasoline, there is a reduced smog formation from evaporative emissions in pure ethanol [181]. Bioethanol can also be conveniently blended with gasoline to improve the octane number as well as to promote a more complete combustion. The power output of the engine fueled with low ethanol/gasoline blends is higher compared to gasoline-fueled engines. In general, 10% ethanol addition increases the engine power output by 5%. However, even for low percentage ethanol/gasoline blends (e.g. 10%), undesirable interactions between ethanol and gasoline may cause the vapor pressure to increase. To compensate this effect, the vapor pressure of the gasoline may be reduced. Bioethanol has a very low toxicity compared to other petroleum-based fuels and is readily biodegradable in water and soils (>70% biodegradable compared to diesel fuel), reducing the penetration of plumes of smoke from leaks and environmental concerns as a consequence of spills.

8.3.2.1 Effect of Bioethanol on Diesel Engines Performance Properties

Alcohols can enhance the combustion in compression ignition engines. There are a number of fuel properties that are essential for the optimum performance of a diesel engine. The addition of ethanol to diesel fuel may affect key properties of the blend with particular reference to blending stability, viscosity and lubricity, energy content and cetane number. The properties of ethanol–diesel fuel blends have a significant effect on safety, engine performance, durability, and emissions [177].

Homogeneous charge compression ignition (HCCI) engines tipically exhibit a rapid combustion. However, the components in fuel mixtures do not ignite in unison or burn equally. The combustion of fuel blends in HCCI engines may find a preferential combustion of some the components of the blend [182].

The aromatic content of diesel fuel can also affect the solubility of ethanol in its blend and therefore the effectiveness of emulsifiers and co-solvents [183]. The polar nature of ethanol induces a dipole in the aromatic molecule allowing it to interact with the ethanol, while the aromatics remain compatible with other hydrocarbons in diesel fuel.

The addition of ethanol to diesel lowers the viscosity and lubricity of the final blend. Lower fuel viscosities lead to greater pump and injector leakage, reducing maximum fuel delivery and ultimately power output. Hot restart problems may occur also as a consequence of the insufficient fuel injected at cranking speed (when fuel leakage in the high-pressure pump is amplified) due to the reduced viscosity of the hot fuel. Fuel viscosity also affects the atomization and spray characteristics in the combustion chamber [184].

With the inverse relationship of octane number and cetane number, ethanol exhibits a low cetane rating (inferior to 10). Hence, increasing concentrations of ethanol in blends proportionately lower the cetane number.

An increase in fuel consumption approximately equivalent to the reduction in energy content of the fuel can also be expected when using ethanol/diesel fuel blends. The energy content in the blends decreases by approximately 2% for each 5% of ethanol added, by volume, assuming that any additive included in the blend has the same energy content as diesel fuel [185]. In any case, no noticeable differences in engine performance, compared to diesel fuel, have been reported with ethanol contents up to 10% [186].

8.3.2.2 Effect of Bioethanol on Spark Ignition Engines Performance Properties

Extensive research efforts have been devoted to investigate the effect of ethanol as a pure fuel and its blends with gasoline on engine performance [187]. Currently, the ethanol consumption in the Brazilian transportation sector represents 44% of the overall gasoline consumption used for transport [188]. Nevertheless, the use of ethanol and ethanol-gasoline blends on spark ignition engines may originate some problems. Upon increasing the ethanol content in the fuel (up to 10%), the heating value of the blends decreases and then the Reid vapor pressure (RVP, a common measure of the volatility of gasoline) increases (which indicates indirectly increased evaporative emissions, while CO tailpipe decreases) to a maximum and then decreases. The heating value of ethanol is lower than gasoline. Therefore, in order to achieve the same energy output, 1.5–1.8 times more ethanol is needed. This leads to higher volumetric fuel consumption compared to petrol, which causes an increase of the BSFC [174]. Other problem related to the use of ethanol-gasoline blends is the phase separation, in the presence of water. Alcohols with 3–8 carbon atoms have better water solubility in blends [189].

Bioethanol has a higher octane rating mixture than branched alcohols, but is far more volatile owing to the formation of minimum temperature azeotropes with the hydrocarbons of gasoline and thus presenting a higher vapor pressure than mixtures of ethers in gasoline [190].

The rapidly increasing use of ethanol as a biofuel in blends with gasoline provides an opportunity to expand its further use as petrol-fuel replacement, with the potential to expand markets for agricultural commodities used to produce ethanol.

However further work is required in specifying acceptable fuel characteristics, confirming the long-term effects on engine durability, and ensuring safety in handling and storing ethanol-diesel blends [177].

8.3.2.3 Engine Exhaust Emissions Using Bioethanol

Bioethanol used in combustion engines has a tremendous potential for a net reduction in the emissions of greenhouse gases. Life-cycle emissions predict the great environmental benefit that can be achieved from the use of bioethanol as transport fuel. Ethanol and others biofuels are considered as "climate friendly", even when considered on a life-cycle basis [191, 192].

CO_2 is released into the atmosphere when a fuel is burned in the engine. However, it is recycled into organic tissues during plant growth. Only about 40% or less of the organic matter is actually removed from farm fields for ethanol production [174]. Bioethanol is believed to give a 70% carbon dioxide reduction compared to petrol [51].

CO is formed by the incomplete combustion of fuels, most readily produced from petroleum fuels, which contain no oxygen in their molecular structure. Since ethanol and other oxygenated compounds contain oxygen, their combustion in automobile engines is more complete. The result is a substantial reduction in CO emissions (up to 30%), depending on the type and age of engine/vehicle, the emission control system used, and the atmospheric conditions in which the vehicle operates.

The addition of bioethanol to diesel fuel has also a beneficial effect in reducing particulate matter (PM) emissions [193]. The degree of improvement varies from engine to engine and also within the working range of the engine itself. While there is considerable value in being able to use the fuel directly in an unmodified engine, small adjustments to fuel injection characteristics may result in further gains in reducing emissions [177].

Because of its high octane number, the addition of bioethanol to gasoline leads to the reduction or removal of aromatic hydrocarbons (e.g. benzene), and other hazardous high-octane additives commonly used to replace tetraethyl lead in gasoline [194]. Clear trends of reduced hydrocarbons and CO emissions and increased NO_x emissions have been observed with increasing percentages of ethanol in the blend (from 0 to 20%). A standard vehicle operates at air/fuel ratios significantly richer than stoichiometric, with an average air/fuel ratio running on gasoline of approximately 12.2:1. For leaner base conditions, the trend could be the opposite, with increasing hydrocarbon emissions and reduced NO_x emissions with increasing ethanol contents [195]. Acetaldehyde emissions are also superior with increasing ethanol contents in the blend as this compound can be produced from ethanol via oxidation under certain operating conditions. Interestingly, such emissions have also a close relationship with the engine load and the ethanol content in the blend. With increasing loadings from idling, the acetaldehyde emissions gradually decrease to their minimum at medium loads, then increase again at high engine loads [192].

Toxic unregulated emissions (i.e. formaldehyde, propionaldehyde, 1,3-butadiene, acrolein, linear alkenes and aromatics) and fine particulate should be considered to ascertain the impact of ethanol-blended fuels. Researchers report benzene emissions reduction up to 50% with the ethanol-blended fuels. Emissions of 1,3-butadienes were also substantially decreased in the range from 24 to 82% [196].

8.3.3 Effect of Ethers as Biofuels in Spark Ignition Engine Performance Properties

The industrial production of tert-alkyl ethers has a rising interest for refineries, due to reformulated gasoline obtained with respect to EURO standards applied in Europe, Australia and New Zealand [197]. The asymmetric ethers are synthesized through an addition reaction between the alcohols and the tertiary olefins of high reactivity which may be found in the hydrocarbons flow coming out of destructive processes such as catalytic cracking and pyrolysis [197]. In this way, ethers including ETBE (C_4H_9–O–C_2H_5), and TAEE (C_5H_{11}–O–C_2H_5) can be prepared as alternative fuels. In France, Spain and Germany, ETBE is usually mixed with gasoline in proportions up to 15 vol% [198]. It is produced by the etherification of isobutene, usually present in a mixture of C4 isomers, with ethanol [188, 190, 197, 198]. ETBE is an adequate substitute for methyl tert-butyl ether (MTBE), an oxygenating additive that is currently prohibited in many countries due to its toxicity and contamination of underground waters [199]. These ethers offer several advantages with respect to ethanol in terms of low latent heat of vaporization, low solubility in water and higher combustion enthalpy [200].

8.4 Future Prospects and Challenges

8.4.1 Future Prospects: 1st Vs 2nd Generation Biofuels

Various interesting conclusions can be drawn from the use of first and second generation biofuels. 1st generation biodiesel and bioalcohols have many advantages as petrol-fuel replacements but also important disadvantages. The main concern related to the production of first generation biofuels comes from the fact that the conventional biofuel production process generally involves the use of ‘food’ crops. This issue has generated much controversy in a world where the limited area of arable land and grain reserves may contribute to skyrocket the food prices if we carry on using such food crops extensively for biofuel production. That and other issues that arise related to deforestation, global warming and biodiversity threatening, in particular in developing countries (e.g. Malaysia as a consequence of the use of vegetable oils (e.g. palm oil) for the production of biodiesel) encouraged the search for alternative technologies and feedstocks for biofuels production and the development of second generation biofuels.

The production of biofuels from second generation biofuels from non-edible feedstocks has interesting features. Non food crops can be cultivated in alternative lands included the so-called “wastelands”, tropical zones or even arid regions as they are more likely to proliferate at relatively extreme conditions (e.g. plagues and dry environments) with a low fertiliser input. Many of the biomass feedstocks are also self-seeding crops (they do not need to be planted and re-seeded after harvested) and require little or virtually no fertilizer input. These approaches can therefore be applied to “marginal lands” where the soil cannot/should not support food crops [201]. In this way, they will not interfere with the land dedicated to food crops. They can also provide a solution for the production of quality biofuels in developing countries (e.g. India) where, for example, a blend of biodiesel obtained from jatropha and palm has been reported to have a right balance of physical properties conferring the product with an adequate cold low performance and oxidation stability [62], also falling within the acceptable by the American and European biodiesel standards.

However, the switch to these non-edible feedstocks poses various concerns. The cultivation patterns of the crops are still under investigation and early studies have shown relative differences depending on the approach taken to crop cultivation and oil production management [202]. The crops have only been employed by local communities for different uses (e.g. soap production and natural crop protection for the inedible nature of the oil and toxicity of the seeds, respectively) [203, 204]. Therefore, the evaluation of the sustainability index needs of more data to estimate the real global impact of these crops. Furthermore, the technologies available for the majority of the second generation biofuels are still in their infancy and need major developments to be able to sustain a scaled-up production of biofuels for transport. The economics of the processes may play a key role in the successful implementation of many of these technologies.

A full discussion on these important topics, with a thorough evaluation of socio-economic, environmental and related issues, has been recently reported [205]. Some of the most relevant prospects and challenges for the future of second generation biofuels will now be detailed.

8.4.1.1 Second Generation Biodiesel

The use of cheap feedstocks (e.g. waste oils and fats) and the potential commercialisation of glycerol (and glycerol derived products) can considerably reduce the biodiesel production costs, specially taking into account that 70–90% of the biodiesel cost arises from the cost of the oil [206]. However, the use of high temperatures in the transesterification, incomplete conversion and variability of the incoming feedstock (with marked differences in water content and FFA depending on the source, location and usage) are problems related to such feedstocks for biodiesel production.

The production of methyl esters from algal oil has also recently attracted a great deal of attention. The enormous diversity of species of algae with high oil content that require a tiny land utilisation compared to oil crops offers an interesting possibility of industrial exploitation of such organisms in the production of biodiesel.

However, there are major limitations in their successful implementation, being the economic feasibility of the technology the most important. Firstly, the recovery of such bio-oil from algae is very challenging task. The algal broth produced in the biomass production generally needs to be further processed to recover the biomass [207] and then the concentrated biomass paste is extracted with an organic solvent (e.g. hexane) to recover the algal oil that can be transesterified into biodiesel.

Secondly, microalgal oil is rich in long-chain polyunsaturated acids including eicosapentaenoic (20:5 n-3, EPA) and docosahexaenoic acids (22:6 ω-3, DHA) which are generally undesirable in conventional biodiesel due to the negative impact of the polyunsaturations on oxidation stability. The presence of EPA and DHA is not contemplated in the EU (EN 14214 and EN 14213, biodiesel for transport and heating) and US (ASTM D6751) quality biodiesel standards that specify a limit of 130 g (EN 14213) and 120 g (EN 14214) iodiene/100 g biodiesel (iodine value). The storage issues arising from the oxidation instability may either be overcome through chemical transformations (e.g hydrogenations) of the polyunsaturated compounds [208]. It is yet unclear how the presence much more saturated FAME will affect cold performance (CFPP) of the biodiesel.

These main drawbacks will undoubtedly put up the costs of an already costly process in which problems related to capital infrastructure costs, contamination through open pond systems and costs associated with harvesting, drying and valorisation of the rest of the algae may have also a major contribution. A full and precise estimation of the economics of the process, that have been argued to be far too good from what Chisti [74, 75] originally reported, is needed in order to demonstrate its feasibility [76, 207].

8.4.1.2 Second Generation Bioalcohols

There are two critical issues that need to be addressed for the succesful development of the second generation bioalcohols from biomass via biological conversion. Firstly, the development of an efficient pre-treatment process in order to break up the fibre structure of the biomass is needed because the methodologies investigated (mechanical, thermal, chemical, enzymatic-cellulase- and combinations of them) have been proven to be unsuitable due their high costs, low yields, produced waste or undesired by-products. Secondly, an efficient microorganism for the fermentation of pentoses, present in hemicellulose, needs to be developed. These strategies may also open up interesting possibilities to employ more user-friendly microorganisms (e.g. *Saccharomyces cerevisiae*) for biofuels production. Therefore, there is a need for a joint effort from chemists, microbiologists and chemical and biochemical engineers in order to demonstrate the potential of second generation bioethanol via biological conversion.

Bioalcohols obtained from the gasification of biomass does not have significant differences in properties compared to that obtained by biological conversion. However, the processes are remarkably dissimilar. The conventional gasification step is a costly process compared to the relatively inexpensive biological conversion. Another important issue that needs to be addressed is the lack of standards for producers and users. Nevertheless, the biomass feedstock can effectively be turned into syngas (without the need of any microorganisms) and subsequently into bioalcohols [3]. Compared to bioalcohols produced by biological conversion, this protocol avoids issues such as the inefficient degradation of biomass to fermentable sugars as well as dealing with the processing of the pentoses (C5) generated in the hydrolysis of biomass.

8.4.1.3 Biogas

Biogas might be of relevance in renewable energy markets both for transport and for generation of electricity. It is also a realistic alternative to the accumulation of waste in landfill as new sites can be specially configured to optimise gas output (as high as 1000 m^3/h biogas. However, LCA studies have identified an impact to GHG in its production, associated to the generation and emission of CO_2 and N_2O in the process [126, 127].

8.4.1.4 Biohydrogen

Biohydrogen is believed to be one of the biofuels for the future, combining its ability to potentially reduce the dependence of foreign oil and contribute to lower the GHG emissions from the transportation sector. However, storage (biohydrogen has to be compressed, liquefied, or stored in metal hydrides), transportation and use (fuel cell vehicles are not commercially available yet and a distribution infrastructure for hydrogen cannot be realised in the short term) as well as the technological advances needed for its successful implementation limit bio-hydrogen only as a longer-term option for the transport sector.

8.4.1.5 Bio-SNG

Bio-SNG has various advantages but also a number of challenges for the future. Its octane number is very high, but the cetane number is very low, which means that bio-SNG has to be used in spark ignition engines, which need to be adapted for its use. Storage is also a challenge for the future as bio-SNG is also a gas at room temperature so it needs to be compressed or liquefied to be used as an automotive fuel. Furthermore, larger storage and fuel tanks are needed due to the lower volumetric energy content of the fuel.

The supercritical water low-temperature gasification technology may overcome some of the main technological barriers in the process. Nevertheless, gas cleaning (especially tar removal) and catalyst development are important technological issues, although if active and selective catalysts are used (e.g. Ru/C), no significant quantities of tars or char have been reported to form. However, the cost of the supercritical water production of bio-SNG is several times higher than that of the conventional gasification process [89].

8.4.1.6 Synthetic Biofuels

Synthetic biofuels have several advantages as they can be used in unmodified diesel engines [88, 89] and they are cleaner that traditional fuels due to the removal of all contaminants to avoid the poisoning of the catalysts used in the processing steps [3, 105, 106]. These biofuels can have excellent autoignition characteristics as they have similar energy content, density and viscosity that of fossil diesel as well as higher cetane number and lower aromatic content (which results in lower particle emissions). They are also S-, N-free and less corrosive than other biofuels (e.g. bioethanol and biodiesel) therefore being more environmentally friendly than fuels produced from crude oil. Some of them (e.g. FT-diesel) have been proved to reduce the CO, NOx and particulate matter compared to diesel fuel [88, 107, 108].

However, the production of synthetic biofuels faces a similar technological barrier to that of the gasification-derived biofuels (i.e. bioalcohols and other synthetic biofuels): the production of the synthesis gas has to be adapted to the higher reactivity and different properties of biomass with respect to coal. This includes two key steps in the process that need thorough improvements: biomass pre-treatment (via torrefaction and/or pyrolysis) to avoid the aggregation of the biomass particles that can plug the feeding lines and economically viable inferior temperatures of gasification (e.g. *via* supercritical water gasification) that have been reported to provide higher efficiencies.

For instance, the FTS biofuel production can be more cost effective reducing both the capital and the operating costs of the plant [209], being the purification of the syngas the most expensive section to take into account for costs in an FT plant. The development of active and selective catalysts and the utilisation of by-products including electricity, heat and steam are some other inputs that need to be addressed.

8.5 Conclusions

The potential for biofuels has been recognised throughout the twentieth century but the new century has brought with it a widespread realisation that the petroleum age is coming to an end. The use of petrol-fuel replacements has generated a lot of controversy; ideally they should contribute to global sustainability, ensuring the energy supply and meeting the GHG targets (as well as being profitable and cost competitive as much as possible) without compromising the economies, culture, societies and the environment of our future. More thoughtful analysis is now showing that many of these so-called first generation biofuels are little better than traditional fuels in terms of overall carbon footprint and environmental damage. Second generation biofuels and more widely, biomass exploitation, have a great potential to improve these values and the future aims should focus on redoubling our efforts to produce later generation biofuels based on low value and waste biomass, using the greenest and efficient technologies and with properly measured and reported environmental impacts. A joint effort from politics, economists, environmentalists and scientists is needed now, more than ever, to address the issues of the progressive incorporation of biofuels in our society and to come up with alternatives, policies and choices to advance the key technologies for a more sustainable future.

Acknowledgments Authors greatly acknowledge funds from Ministerio de Ciencia e Innovación (Projects CTQ2007-65754/PPQ, CTQ2008-01330/BQU, ENE2007-65490/ALT and HI2008-0229), Spanish International Cooperation Agency AECID (project PCI-C/019212/08) and Junta de Andalucía (FQM-191, TEP-169 and P07 FQM-02695), cofinanced with FEDER funds.

References

1. IPCC (2007a) in: Solomon, S, Qin, D, Manning, M, Chen, Z, Marquis, M, Averyt, KB, Tignor, M & Miller, HL (Eds), Climate Change 2007: The Physical Science Basis. Contribution of Working Group 1 to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, Cambridge University Press, Cambridge, UK/ New York.
2. IPCC (2007b) in: Metz, B, Davidson, OR, Bosch, PR, Dave, R & Meyer, LA (Eds), Climate change 2007: Mitigation. Contribution of Working Group 3 to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, Cambridge University Press, Cambridge, UK/New York.
3. The Royal Society (2008), Sustainable biofuels: Prospects and challenges, ISBN 978 0 85403 662 2.
4. IEA (2007) World Energy Outlook 2007, International Energy Agency, Paris.
5. Ford Runge, C., Senauer, B. (2007) How biofuels could starved the poor. *Foreign Affairs*, 86 (3) http://www.foreignaffairs.org/20070501faessay86305-p10/c-ford-runge-benjamin-senauer/how-biofuels-could-starve-the-poor.html
6. Hazell, P., Pachauri, R.K. (Eds.) Bioenergy and Agriculture: Promises and challenges, International Food Policy Research Institute 2020 Focus No14, 2006.
7. Demirbas, A. (2008) The importance of bioethanol and biodiesel from biomass. *Energy Sources Part B: Economics, Planning and Policy*, 3, 177–185.
8. Rothenberg, G. (2008) Catalysis; Concepts and Green Applications, Wiley-VCH, Weinheim.
9. Demirbas, A. (2005) Biodiesel production from vegetable oils via catalytic and non-catalytic supercritical methanol transesterification methods. *Progress in Energy and Combustion Science*, 31, 466–487.
10. Kammen, D.M., Kapadia, K., Fripp, M. (2004) “Putting Renewables to Work: How Many Jobs Can the Clean Energy IndustryGenerate?” Report of the Renewable and appropriate Energy Laboratory, University of California Berkeley.
11. Pimentel, D., Patzek, T.W. (2005) Ethanol production using corn, switchgrass, and wood; biodiesel production using soybean and sunflower. *Natural Resources Research*, 14, 65–76.
12. Marchetti, J.M., Miguel, V.U., Errazu, A.F. (2007) Possible methods for biodiesel production. *Renewable Sustainable Energy Reviews*, 11, 1300–1311.
13. Vicente, G., Martinez, M., Aracil, J. (2006) A comparative study of vegetable oils for biodiesel production in Spain. *Energy & Fuels*, 20, 394–398.
14. Pinto, A.C., Guarieiro, L.L.N., Rezende, M.J.C., Ribeiro, N.M., Torres, E.A., Lopes, W.A., Pereira, P.A.P., de Andrade, J.B. (2005) Biodiesel: An overview. *Journal of the Brazilian Chemical Society*, 16, 1313–1330.
15. Mittelbach, M., Remschmidt, C. (Eds.) (2005) Biodiesel, the Comprehensive Handbook, 2nd (Ed.) Martin Mittelbach, Austria.
16. Al-Zuhair, S. (2007) Production of biodiesel: Possibilities and challenges. *Biofuels Bioproducts Biorefining*, 1, 57–66.
17. Mittelbach, M., Wörgetter, M., Pernkopf, J., Junek, H. (1983) Diesel fuel derived from vegetable oils: Preparation and use of rape oil methyl ester. *Energy and Agriculture*, 2, 369–384.
18. Vicente, G., Martinez, M., Aracil, J. (2004) Integrated biodiesel production: A comparison of different homogeneous catalysts systems. *Bioresource Technology*, 92, 297–305.

19. Noureddini, H., Zhu, D. (1997) Kinetics of transesterification of soybean oil. *Journal of the American Oil Chemical Society*, 74, 1457–1463.
20. Antolin, G., Tinaut, F.V., Briceno, Y., Castano, V., Perez, C., Ramirez, A.I. (2002) Optimisation of biodiesel production by sunflower oil transesterification. *Bioresource Technology*, 83, 111–114.
21. Ruiz-Méndez, M.V., Marmesat, S., Liotta, A., Dobarganes, M.C. (2008) Analysis of used frying fats for biodiesel production. *Grasas y Aceites*, 59, 45–50.
22. Freedman, B., Butterfield, R.O., Pryde, E.H. (1986) Transesterification kinetics of soybean oil. *Journal of the American Oil Chemical Society*, 63, 1375–1380.
23. Zheng, S., Kates, M., Dubé, M.A., McLean, D.D. (2006) Acid-catalyzed production of biodiesel from waste frying oil. *Biomass and Bioenergy*, 30, 267–272.
24. Lotero, E., Liu, Y., Lopez, D.E., Suwannakarn, K., Bruce, D.A., Goodwin, J.G., Jr. (2005) Synthesis of biodiesel via acid catalysis. *Industrial & Engineering Chemical Research*, 44(23), 5353–5363.
25. Schuchardt, U., Sercheli, R., Vargas, R.M. (1998) Transesterification of vegetable oils: A review. *Journal of the Brazilian Chemical Society*, 9(3), 199–210.
26. Cerce, T., Peter, S., Weidner, E. (2005) Biodiesel-transesterification of biological oils with liquid catalysts: Thermodynamic properties of oil-methanol-amine mixtures. *Industrial & Engineering Chemical Research*, 44(25), 9535–9541.
27. Ono, T., Yoshibaru, K. *US Pat*. 1979, 4,164,506.
28. Di Serio, M., Tesser, R., Pengmei, L., Santacesaria, E. (2008) Heterogeneous catalysts for biodiesel production. *Energy & Fuels*, 22, 207–217.
29. Verziu, M., Cojocaru, B., Hu, J., Richards, R., Ciuculescu, C., Filip, P., Parvulescu, V.I. (2008) Sunflower and rapeseed oil transesterification to biodiesel over different nanocrystalline MgO catalysts. *Green Chemistry*, 10, 373–381.
30. Chen, H., Wang, J.F. (2006) Biodiesel from transesterification of cottonseed oil by heterogeneous catalysis. *Studies in Surface Science and Catalysis*, 159, 153–156.
31. Suppes, G.J., Bochwinkel, K., Lucas, S., Botts, J.B., Mason, M.H., Heppert, J.A. (2001) Calcium carbonate catalyzed alcoholysis of fats and oils. *Journal of the American Oil Chemists Society*, 78, 139–145.
32. Vicente, G., Coteron, A., Martinez, M., Aracil, J. (1998) Application of the factorial design of experiments and response surface methodology to optimize biodiesel production. *Industrial Crops and Production*, 8(1), 29–35.
33. Kim, H.J., Kang, B.S., Kim, M.J., Park, Y.M., Kim, D.K., Lee, J.S., Lee, K.Y. (2004) Transesterification of vegetable oil to biodiesel using heterogeneous base catalyst. *Catalysis Today*, 93–95, 315–320.
34. Ma, H., Li, S., Wang, B., Wang, R., Tian, S. (2008) Transesterification of rapeseed oil for synthesizing biodiesel by K/KOH/ γ-Al_2O_3 as heterogeneous base catalyst. *Journal of the American Oil Chemists Society*, 85, 263–270.
35. Leclercq, E., Finiels, A., Moreau, C. (2001) Transesterification of rapeseed oil in the presence of basic zeolites and related solid catalysts. *Journal of the American Oil Chemists Society*, 78, 1161–1165.
36. Toda, M., Takagaki, A., Okamura, M., Kondo, J.N., Hayashi, S., Domen, K., Hara, M. (2005) Green chemistry: Biodiesel made with sugar catalyst. *Nature*, 438, 178.
37. MacLeod, C.S., Harvey, A.P., Lee, A., Wilson, K. (2008) Evaluation of the activity and stability of alkali-doped metal oxide catalysts for application to an intensified method of biodiesel production. *Chemical Engineering Journal*, 135(1–2), 63–70.
38. Hsu, A.F., Jones, K., Foglia, T.A., Marmer, W.N. (2002) Immobilized lipase-catalysed production of alkyl esters of restaurant grease as biodiesel. *Biotechnology and Applied Biochemistry*, 36, 181–186.
39. Tan, T., Yin, C (2005) The mechanism and kinetic model for glycerolysis by 1,3 position specific lipase from Rhizopus arrhizus. *Biochemical Engineering Journal*, 25(1), 39–45.

40. Macario, A., Giordano, G., Setti, L., Parise, A., Campelo, J.M., Marinas, J.M., Luna, D. (2007) Study of lipase immobilization on zeolitic support and transesterification reaction in a solvent free-system. *Biocatalysis and Biotransformation*, 25, 328–335.
41. Sanchez, F., Vasudevan, P.T. (2006) Enzyme catalyzed production of biodiesel from olive oil. *Applied Biochemistry and Biotechnology*, 135(1), 1–14.
42. Yagiz, F., Kazan, D., Akin, N.A. (2007) Biodiesel production from waste oils by using lipase immobilized on hydrotalcite and zeolites. *Chemical Engineering Journal*, 134, 262–267.
43. Caballero, V. Bautista, F.M., Campelo, J.M., Luna, D., Marinas, J.M., Romero, A.A., Hidalgo, J.M., Luque, R., Macario, A., Giordano, G. (2009) Sustainable preparation of a novel glycerol-free biofuel by using pig pancreatic lipase: Partial 1,3-regiospecific alcoholysis of sunflower oil. *Process Biochemistry*, 44(3), 334–342.
44. Watanabe, Y., Pinsirodom, P., Nagaoa, T., Yamauchi, A., Kobayashi, T., Nishida, Y., Takagi, Y., Shimada, Y. (2007) Conversion of acid oil by-produced in vegetable oil refining to biodiesel fuel by immobilized Candida antarctica lipase. *Journal of Molecular Catalysis B: Enzymatic*, 44(3–4), 99–105.
45. Houde, A., Kademi, A., Leblanc, D. (2004) Lipases and their industrial applications. An overview. *Applied Biochemistry and Biotechnology*, 118, 155–170.
46. Sharma, R., Chisti, Y., Banerjee, U.C. (2001) Production, purification, characterization, and applications of lipases. *Biotechnology Advances*, 19, 627–662.
47. Demirbas, A. (2002) Biodiesel from vegetable oils via transesterification in supercritical methanol. *Energy Conversion and Management*, 43, 2349–2356.
48. Sawangkeaw, R., Bunyakiat, K., Ngamprasertsith, S. (2007) Effect of co-solvents on production of biodiesel via transesterification in supercritical methanol. *Green Chemistry*, 9(3), 679–685.
49. http://siteresources.worldbank.org/INTWDR2008/Resources/2795087-1192112387976/WDR08_05_Focus_B.pdf.
50. Draye, X., Lin, Y.R., Qian, X.Y., Bowers, J.E., Burow, G.B., Morrell, P.L., Peterson, D.G., Presting, G.G., Ren, S.X., Wing, R.A., Patterson, A.H. (2001) Toward integration of comparative genetic, physical, diversity, and cytomolecular maps for grasses and grains, using the sorghum genome as a foundation. *Plant Physiology*, 125(3), 1325–1341.
51. Balat, M., Balat, H., Oz, C. (2008) Progress in bioethanol processing. *Progress in Energy and Combustion Science*, 34, 551–573.
52. Gray, K.A., Zhao, L., Emptage, M. (2006) Bioethanol. *Current Opinion in Chemical Biology*, 10(2), 141–146.
53. Dürre, P. (2007) Biobutanol: An attractive biofuel. *Biotechnology Journal*, 2(12), 1525–1534.
54. Dürre, P. (2008) Fermentative butanol production: Bulk chemical and biofuel. *Annals of the New York Academy of Sciences*, 1125, 353–362.
55. Ezeji, T.C., Qureshi, N., Blaschek, H.P. (2007) Bioproduction of butanol from biomass: From genes to bioreactors. *Current Opinion in Biotechnology*, 18(3), 220–227.
56. Cascone, R. (2007) Biofuels: What is beyond ethanol and biodiesel?. *Hydrocarbon Processing*, 86, 95–109.
57. Antoni, D., Zverlov, V.V., Schwarz, W.H. (2007) Biofuels from microbes. *Applied Microbiology and Biotechnology*, 77, 23–35.
58. http://www2.dupont.com/Biofuels/en_US/
59. http://www.biofuelsmedia.com/news_link.php?new=55.
60. http://www.butanol.com/index.html.
61. Plass, L., Reimelt, S. (2007) Second generation biofuels. *Hydrocarbon Engineering*, 12(6), 71–74.
62. Sarin, R., Sharma, M., Sinharay, S., Malhotra, R.K. (2007) Jatropha-Palm biodiesel blends: An optimum mix for Asia. *Fuel*, 86(10–11), 1365–1371.
63. Achten, W.M.J., Mathijs, E., Verchot, L., Singh, V.P., Aerts, R., Muys, B. (2007) Jatropha biodiesel fueling sustainability? *Biofuels, Bioproducts and Biorefining*, 1, 283–291.

64. Dorado, M.P., Ballesteros, E., Lopez, F.J., Mittelbach, M. (2004) Optimization of Alkali-Catalyzed transesterification of brassica carinata oil for biodiesel production. *Energy & Fuels*, 18, 77–83.
65. Bouaid, A., Diaz, Y., Martinez, M., Aracil, J. (2005) Pilot plant studies of biodiesel production using Brassica carinata as raw material. *Catalysis Today*, 106(1–4), 193–196.
66. Dittrick, P. (2007) Oil industry researching nonfood biofeedstocks. *Oil & Gas Journal*, 105(29), 20–26.
67. Simpson-Holley, M., Evans, G. (2007) Fueling the end of the oil age. *Outlook Pest Management*, 18(3), 109–113.
68. Berchmans, H.J., Hirata, S. (2008) Biodiesel production from crude Jatropha curcas L. seed oil with a high content of free fatty acids. *Bioresource Technology*, 99(6), 1716–1721.
69. http://www.renewableenergyworld.com/rea/news/story?id=49611.
70. Wang, Y., Ou, S., Liu, P., Xue, F., Tang, S. (2006) Comparison of two different processes to synthesize biodiesel by waste cooking oil. *Journal of Molecular Catalysis A*, 252(1–2), 107–112.
71. Zong, M., Duan, Z.Q., Lou, W.Y., Smith, T.J., Wu, H. (2007) Preparation of a sugar catalyst and its use for highly efficient production of biodiesel. *Green Chemistry*, 9, 434–437.
72. Kulkarni, M.G., Gopinath, R., Meher, L.C., Dalai, A.K. (2006) Solid acid catalyzed biodiesel production by simultaneous esterification and transesterification. *Green Chemistry*, 8, 1056–1062.
73. Tashtoush, G.M., Al-Wydian, M.I., Al-Jarrah, M.M. (2004) Experimental study on evaluation and optimization of conversion of waste animal fat into biodiesel. *Energy Conversion and Management*, 45(17), 2697–2711.
74. Chisti, Y. (2008) Biodiesel from microalgae beats bioethanol. *Trends in Biotechnology*, 26(3), 126–131.
75. Chisti, Y. (2007) Biodiesel from microalgae. *Biotechnology Advances*, 25, 294–306.
76. Carlsson, A.S., Van Bilein, J.B., Möller, R., Clayton, D., Bowles, D. (2002) Micro-and Macroalgae utility for industrial application, Outputs from EPOBIO Project, CPL Press, Berks.
77. http://www.shell.com/home/content/media-en/news_and_library/press_releases/2007/biofuels_cellana_11122007.html
78. Zhu, L.Y., Zong, M.H., Wu, H. (2008) Efficient lipid production with Trichosporon fermentans and its use for biodiesel preparation. *Bioresource Technology*, 99, 7881–7885.
79. Angerbauer, C., Siebenhofer, M., Mittelbach, M., Guebitz, G.M. (2008) Conversion of sewage sludge into lipids by Lipomyces starkeyi for biodiesel production. *Bioresource Technology*, 99, 3051–3056.
80. Papanikolaou, S., Galiotou-Panayotou, M., Fakas, S., Komaitis, M., Aggelis, G. (2007) *European Journal of Lipid Science and Technology*, 109(11), 1060–1070.
81. Huber, G.W., Corma, A. (2007) Synergies between bio- and oil refineries for the production of fuels from biomass. *Angewandte Chemie International Edition*, 46(38), 7184–7201.
82. Chheda, J.N., Huber, G.W., Dumesic, J.A. (2007) Liquid-phase catalytic processing of biomass-derived oxygenated hydrocarbons to fuels and chemicals. *Angewandte Chemie International Edition*, 46(38), 7164–7183.
83. Rajagopal, D., Zilberman, D. Policy Research Working paper 4341 (WPS4341), The World Bank, Sept. 2007.
84. http://iv2s.rastaf.net/errichtung-und-demonstrationsbetrieb-einer-biosngtankstelle/_/prog1/subprog26/project350?MyDic_action=set_langid;langid=2
85. http://www.bio-sng.com.
86. Vogel, F., Waldner, M.H., Rouff, A.A., Rabe, S. (2007) Synthetic natural gas from biomass by catalytic conversion in supercritical water. *Green Chemistry*, 9, 616–619.
87. Bridgwater, A.V. (2003) Renewable fuels and chemicals by thermal processing of biomass. *Chemical Engineering Journal*, 91(2–3), 87–102.
88. http://www.iec.tu-freiberg.de/conference/conf07/pdf/7.1.pdf

89. Demirbas, A. (2007) Progress and recent trends in biofuels. *Progress in Energy and Combustion Science*, 33, 1–18.
90. Nakagawa, H.; Harada, T.; Ichinose, T.; Takeno, K., Matsumoto, S., Kobayashi, M., Sakai, M. (2007) Biomethanol production and CO_2 emission reduction from forage grasses, trees, and crop residues. *JARQ*, 41, 173–180.
91. http://www.refuel.eu/biofuels/biomethanol/.
92. http://www.solarix.eu/en/news/33 (accessed December 2008).
93. van Kasteren, J.M.N., Dizdarevic, D., van der Waall, W.R., Guom, J., Verbernem, R. (2005) Bioethanol from syngas. Project number 0456.472.
94. http://www.iogen.ca/.
95. http://www.processum.se/eng/press/filer/FOLDER_eng.pdf.
96. http://powerecalene.com/
97. Demirbas, A. (2008) Biohydrogen generation from organic waste. *Energy Sources Part A: Recovery, Utilization, and Environmental Effects*, 30, 475–482.
98. Demirbas, A. (2004) Hydrogen-rich gas from fruit shells via supercritical water extraction. *International Journal of Hydrogen Energy*, 29, 1237–1243.
99. Bhaskar, T., Sera, A., Muto, A., Sakata, Y. (2008) Hydrothermal upgrading of wood biomass: Influence of the addition of K_2CO_3 and cellulose/lignin ratio. *Fuel*, 87(10–11), 2236–2242.
100. Steinmann, L. (1999) *PCT Int. Pat.*, WO 9915605 A1 19990401
101. http://www.cpi.umist.ac.uk/eminent/Confidential/meeting/RigaMeeting/Riga%20Workshop/March%2008%20HTU%20case.ppt.
102. http://www.refuel.eu/biofuels/htu-diesel/.
103. Dry, M.E. (1996) Practical and theoretical aspects of the catalytic Fischer-Tropsch process. *Applied Catalysis A: General*, 138(2), 319–344.
104. Dry, M.E. (2001) High quality diesel via the Fischer-Tropsch process – a review. *Journal of Chemical Technology and Biotechnology*, 77(1), 43–50.
105. Li, S., Krishnamoorthy, S., Li, A., Meitzner, G.D. Iglesia, E. (2002) Promoted iron-based catalysts for the Fischer-Tropsch synthesis: Design, synthesis, site densities, and catalytic properties. *Journal of Catalysis*, 206(2), 202–217.
106. Schulz, H. (1999) Short history and present trends of Fischer-Tropsch synthesis. *Applied Catalysis A: General*, 186(1–2), 3–12.
107. Alleman, T.L., McCormick, R.L. (2003) *SAE Technical Paper* No. 2003-01-0763
108. Demirbas, A. (2007) Alternatives to petroleum diesel fuel. *Energy Sources Part B: Economics, Planning and Policy*, 2, 343–351.
109. Tijmensen, M.J.A., Faaij, A.P.C., Hamelinck, C.N., van Hardeveld, M.R.M. (2002) Exploration of the possibilities for production of Fischer Tropsch liquids and power via biomass gasification. *Biomass and Bioenergy*, 23(2), 129–152.
110. Russo, G. (2006) Special report: Biofuels: Bio bonanza. *Nature*, 444, 648–649.
111. Tilman, D., Hill, J., Lehman, C. (2006) Carbon-negative biofuels from low-input high-diversity grassland biomass. *Science*, 314, 1598–1600.
112. Lange, J.P. (2007) Lignocellulose conversion: An introduction to chemistry, process and economics. *Biofuels Bioproducts Biorefining*, 1(1), 39–48.
113. Pu, Y., Zhang, D., Singh, M.P., Ragauskas, A.J. (2008) The new forestry biofuels sector. *Biofuels Bioproducts Biorefining*, 2(1), 58–73.
114. Lynd, L.R., Van Zyl, W.H., McBride, J.E., Laser, M. (2005) Consolidated bioprocessing of cellulosic biomass: An update. *Current Opinion in Biotechnology*, 16(5), 577–583.
115. Atsumi, S., Hanai, T., Liao, J.C. (2008) Non-fermentative pathways for synthesis of branched-chain higher alcohols as biofuels. *Nature*, 451, 86–90.
116. Tollefson, J. (2008) Energy: Not your father's biofuels. *Nature*, 451, 880–883.
117. Tollefson, J. (2008) *Chemistry World*, 5(2), 21.
118. Mata-Alvarez, J., Macé, S., Llabrés, P. (2000) Anaerobic digestion of organic solid wastes. An overview of research achievements and perspectives. *Bioresource Technology*, 74, 3–16.
119. Derbimas, A. (2001) *Energy Conversion and Management*, 42, 1375–1378.

120. Ramage, J., Scurlock, J. (1996) in: Biomass, Boyle, G. (Ed.), Renewable Energy-Power for a Sustainable Future, Oxford University Press, Oxford, UK.
121. Demirbas, A. (2008) Biofuels sources, biofuel policy, biofuel economy and global biofuel projections. *Energy Conversion and Management*, 49, 2106–2116.
122. Kapdi, S.S., Vijai, V.K., Rajesh, S.K., Prasad, R. (2005) Biogas scrubbing, compression and storage: Perspective and prospectus in Indian context. *Renewable Energy*, 30(8), 1195–1202.
123. Kuwahara, N., Berni, M.D., Bajay, S.V. (1999) Energy supply from municipal wastes: The potential of biogas-fuelled buses in Brazil. *Renewable Energy*, 16(1–4), 1000–1003.
124. http://www.trendsetter-europe.org/index.php?ID=2842.
125. Lantz, M., Svensson, M., Björnsson, L., Börjesson, P. (2007) The prospects for an expansion of biogas systems in Sweden—Incentives, barriers and potentials. *Energy Policy*, 35(3), 1830–1843.
126. Das, D., Veziroglu, T.N. (2008) Advances in biological hydrogen production processes. *International Journal of Hydrogen Energy*, 33(21), 6046–6057.
127. Melis, A. (2002) Green alga hydrogen production: Progress, challenges and prospects. *International Journal of Hydrogen Energy*, 27(11–12), 1217–1228.
128. Murphy, D.J. (2008) Future prospects for biofuels. *Chimica Oggi*, 26, 14–19.
129. Manish, S., Banerjee, R. (2008) Comparison of biohydrogen production processes. *International Journal of Hydrogen Energy*, 33(1), 279–286.
130. Davila-Vazquez, G., Arriaga, S., Alatriste-Mondragon, F., De Leon-Rodriguez, A., Rosales-Colunga, L.M., Razo-Flores, E. (2008) Fermentative biohydrogen production: Trends and perspectives. *Reviews in Environmental Science and Bio/Technology*, 7(1), 27–45.
131. Ren, N., Li, J., Li, B., Wang, Y., Liu, S. (2006) Biohydrogen production from molasses by anaerobic fermentation with a pilot-scale bioreactor system. *International Journal of Hydrogen Energy*, 31(15), 2147–2157.
132. Zhang, L., Happe, T., Melis, A. (2002) Biochemical and morphological characterization of sulfur-deprived and H_2-producing Chlamydomonas reinhardtii (green alga). *Planta*, 214(4), 552–561.
133. Kaplan, C., Arslan, R., Sürmen, A. (2006) Performance characteristics of sunflower methyl esters as biodiesel. *Energy Sources*, 28, 751–755.
134. Kaufman, K.R., Ziejewski, M. (1984) Sunflower methyl esters for direct injection diesel engines. *Transactions of the ASAE*, 27(6), 1626–1633.
135. Hansen, K.F., Jensen, M.G. (1997) Chemical and biological characteristics of exhaust emissions from a DI diesel engine fuelled with rapeseed oil methyl ester (RME). *SAE paper*, 971689.
136. Çetinkaya, M., Ulusoy, Y., Tekin, Y., Karaosmanoglu, F. (2005) Engine and winter road test performances of used cooking oil originated biodiesel. *Energy Conversion Management*, 46, 1279–1291.
137. Dorado, M.P., Ballesteros, E., Arnal, J.M., Gomez, J., Lopez, F. J. (2003) Exhaust emissions from a diesel engine fueled with transesterified waste olive oil. *Fuel*, 82(11), 1311–1315.
138. Dorado, M.P., Ballesteros, E., Arnal, J.M., Gomez, J., Lopez, F.J (2003) Testing waste olive oil methyl ester as a fuel in a diesel engine. *Energy & Fuels*, 17(6), 1560–1565.
139. Sims, R.E.H. (1985) Tallow esters as an alternative diesel fuel. *Transactions of the ASAE*, 28, 716–721.
140. Staat, F., Vallet, E. (1994) Vegetable oil methyl esters as a diesel substitute. *Chemistry and Industry*, 21, 863–865.
141. Ali, Y., Hanna, M.A., Borg, J.E. (1995) Optimization of diesel, methyl tallowate and ethanol blend for reducing emissions from diesel engine. *Bioresource Technology*, 52, 237–243.
142. Lin, Y.C., Lee, W.J., Wu, T.S., Wang, C.T. (2006) Comparison of PAH and regulated harmful matter emissions from biodiesel blends and paraffinic fuel blends on engine accumulated mileage test. *Fuel*, 85(17–18), 2516–2523.

143. Hasimoglu, C., Ciniviz, M., Oezsert, I., Icinguer, Y., Parlak, A., Sahir Salman, M. (2008) Performance characteristics of a low heat rejection diesel engine operating with biodiesel. *Renewable Energy*, 33(7), 1709–1715.
144. Lapuerta, M., Armas, O., Rodríguez-Fernández, J. (2008) Effect of biodiesel fuels on diesel engine emissions. *Progress in Energy and Combustion Science*, 34(2), 198–223.
145. Carraretto, C., Macor, A., Mirandola, A., Stoppato, A., Tonon, S. (2004) Biodiesel as alternative fuel: Experimental analysis and energetic evaluations. *Energy*, 29(12–15), 2195–2211.
146. Silva, F.N., Prata, A.S., Teixeira, J.R. (2003) Technical feasibility assessment of oleic sunflower methyl ester utilization in diesel bus engines. *Energy Conversion and Management*, 44, 2857–2878.
147. Yücesu, H.S., İlkiliç, C. (2006) Effect of cotton seed oil methyl ester on the performance and exhaust emission of a diesel engine. *Energy Sources*, 28, 389–398.
148. Murillo, S., Miguez, J.L., Porteiro, J., Granada, E., Moran, J.C. (2007) Performance and exhaust emissions in the use of biodiesel in outboard diesel engines. *Fuel*, 86(12–13), 1765–1771.
149. Altiparmak, D., Keskin, A.; Koca, A.; Guerue, M. (2007) Alternative fuel properties of tall oil fatty acid methyl ester-diesel fuel blends. *Bioresource Technology*, 98(2), 241–246.
150. Usta, N. (2005) An experimental study on performance and exhaust emissions of a diesel engine fuelled with tobacco seed oil methyl ester. *Energy Conversion and Management*, 46(15–16), 2373–2386.
151. Monyem, A., Van Gerpen, J.H., Canakci, M. (2001) The effect of timing and oxidation on emissions from biodiesel-fueled engines. *Transactions of the ASAE*, 44(1), 35–42.
152. Kegl, B. (2006) Experimental investigation of optimal timing of the diesel engine injection pump using biodiesel fuel. *Energy & Fuels*, 20, 1460–1470.
153. Kegl, B., Pehan, S. (2008) Influence on biodiesel injection, fuel spray, and engine characteristics. *Thermal Science*, 12(2), 171–182.
154. Sun, X., Wang, W., Bata, R. (1994) Performance evaluation of low heat rejection engines. *Transactions of the ASME*, 116, 758–764.
155. Rakopoulos, C.D., Hountalas, D.T.; Zannis, T. C.; Levendis, Y.A. (2004) Operational and environmental evaluation of diesel engines burning oxygen-enriched intake air or oxygen-enriched fuels: A review. *SAE paper*, 2004-01-2924.
156. Graboski, M.S., Ross, J.D., McCormick, R.L. (1996) Transient emissions from no. 2 diesel and biodiesel blends in a DDC series 60 engine. *SAE paper*, 961166.
157. Turrio-Baldassarri, L., Battistelli, C.L., Conti, L., Crebelli, R., De Berardis, B., Iamiceli, A.L., Gambino, M., Iannaccone, S. (2004) Emission comparison of urban bus engine fueled with diesel oil and biodiesel blend. *Science of the Total Environment*, 327(1–3), 147–162.
158. Canakci, M., Van Gerpen, J.H. (2001) Comparison of engine performance and emissions for petroleum diesel fuel, yellow grease biodiesel, and soybean oil biodiesel. *ASAE Annual international meeting*, 016050.
159. Senatore, A., Caraceni, A., Cioffi, V., Garofalo, F., Vittorioso, G., Barberio, C., Saroglia, G. (2000) A comparative analysis of combustion process in D.I. Diesel engine fueled with biodiesel and diesel fuel. *SAE paper*, 2000–01–0691.
160. Tsolakis, A. (2006) Effects on particle size distribution from the diesel engine operating on RME-biodiesel with EGR. *Energy & Fuels*, 20(4), 1418–1424.
161. Lapuerta, M., Armas, O., Ballesteros, R., Fernandez, J. (2005) Diesel emissions from biofuels derived from Spanish potential vegetable oils. *Fuel*, 84(6), 773–780.
162. Monyem, A., Van Gerpen, J.H. (2001) The effect of biodiesel oxidation on engine performance and emissions. *Biomass and Bioenergy*, 20(4), 317–325.
163. Puhan, S., Vedaraman, N., Sankaranarayanan, G., Ram, B.V.B. (2005) Performance and emission study of Mahua oil (madhuca indica oil) ethyl ester in a 4-stroke natural aspirated direct injection diesel engine. *Renewable Energy*, 30(8), 1269–1278.
164. Hess, M.A., Haas, M.J., Foglia, T.A. (2007) Attempts to reduce NOx exhaust emissions by using reformulated biodiesel. *Fuel Processing Technology*, 88(7), 693–699.

165. Ali, Y., Hanna, M.A. (1994) Alternative diesel fuels from vegetable oils. *Bioresource Technology*, 50(2), 153–163.
166. Chang, D.Y.Z., Van Gerpen, J.H., Lee, I., Johnson, L.A., Hammond, E.G., Marley, S.J. (1996) Fuel properties and emissions of soybean oil esters as diesel fuel. *Journal of American Oil Chemists Society*, 73, 1549–1555.
167. Peterson, C., Reece, D. (1996) Emissions characteristics of ethyl and methyl ester of rapeseed oil compared with low sulfur diesel control fuel in a chassis dynamometer test of a pickup truck. *Transactions of the ASAE*, 39(3), 805–816.
168. Agarwal, A.K., Das, L.M. (2001) Biodiesel development and characterization for use as a fuel in compression ignition engine. *Journal of Engineering for Gas and Turbines Power*, 123, 440–447.
169. Kalligeros, S., Zannikos, F., Stournas, S., Lois, E., Anastopoulos, G., Teas, Ch., Sakellaropoulos, F. (2003) An investigation of using biodiesel/marine diesel blends on the performance of a stationary diesel engine. *Biomass and Bioenergy*, 24(2), 141–149.
170. Manahan, S.E. (2000) Environmental Chemistry, (7th Ed.), Lewis/CRC Press, London/Boca Ratón, FL.
171. Szybist, J.P., Kirby, S.R., Boehman, A.L. (2005) NOx emissions of alternative diesel fuels: A comparative analysis of biodiesel and FT diesel. *Energy & Fuels*, 19(4), 1484–1492.
172. Knothe, G., Sharp, C.A., Ryan, T.W. (2006) Exhaust emissions of biodiesel, petrodiesel, neat methyl esters, and alkanes in a new technology engine. *Energy & Fuels*, 20, 403–408.
173. Mittelbach, M., Tritthart, P. (1988) Diesel fuel derived from vegetable oils, III. Emission tests using methyl esters of used frying oil. *Jounal of the American Oil Chemists Society*, 65(7), 1185–1187.
174. Agarwal, A.K. (2007) Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines. *Progress in Energy and Combustion Science*, 33(3), 233–271.
175. Cardone, M., Prati, M.V., Rocco, V., Seggiani, M., Senatore, A., Vitolo, S. (2002) Brassica carinata as an alternative oil crop for the production of biodiesel in Italy: Engine performance and regulated and unregulated exhaust emissions. *Environmental Science and Technology*, 36(21), 4656–4662.
176. Tat, M.E. (2003) Investigation of Oxides of Nitrogen Emissions from Biodiesel-Fueled Engines, Iowa State University, Ames, IW.
177. Hansen, A.C., Zhang, Q., Lyne, P.W.L. (2005) Ethanol-diesel fuel blends-a review. *Bioresource Technology*, 96(3), 277–285.
178. Balat, M. (2007) Global bio-fuel processing and production trends. *Energy Exploration & Exploitation*, 25(3), 195–218.
179. MacLean, H.L., Lave, L.B. (2003) Evaluating automobile fuel/propulsion system technologies. *Progress in Energy and Combustion Science*, 29(1), 1–69.
180. Nag, A. (2008) Biofuels Refining and Performance, McGraw Hill Professional, New York.
181. Bailey, B.K. (1996) in: Wyman, C.E. (Ed.), Performance of Ethanol as a Transportation fuel in Handbook on Bioethanol: Production and Utilization, Applied Energy Technology Series, Taylor and Francis, London, 37–60.
182. Andrae, J.C.G., Head, R.A. (2009) HCCI experiments with gasoline surrogate fuels modeled by a semidetailed chemical kinetic model. *Combustion and Flame*, 156(4), 842–851.
183. Gerdes, K.R., Suppes, G.J. (2001) Miscibility of ethanol in diesel fuels. *Industrial & Engineering Chemistry Research*, 40(3), 949–956.
184. Heywood, J.B. (1988) Internal Combustion Engine Fundamentals, Publications of McGraw-Hill Inc., New York.
185. Wrage, K.E., Goering, C.E. (1980) Technical feasibility of diesohol. *Transactions of the ASAE*, 23(6), 1338–1343.
186. Hansen, A.C., Hornbaker, R.H., Zhang, Q., Lyne, P.W.L. (2001) On-farm evaluation of diesel fuel oxygenated with ethanol. *ASAE Paper No*. 01-6173. , St. Joseph, MI: ASAE.
187. Wyman, C.E. (2004) in: Cutler, J.C. (Ed.), Ethanol Fuel in Encyclopedia of Energy, Elsevier Inc., New York, 541–555.

188. Cataluña, R., da Silva, R., de Menezes, E.W., Ivanov, R.B. (2008) Specific consumption of liquid biofuels in gasoline fuelled engines. *Fuel*, 87(15–16), 3362–3368.
189. Dagaut, P., Togbe, C. (2008) Oxidation kinetics of butanol-gasoline surrogate mixtures in a jet-stirred reactor: Experimental and modeling study. *Fuel*, 87(15–16), 3313–3321.
190. Pumphrey, J.A., Brand, J.I., Scheller, W.A. (2000) Vapour pressure measurements and predictions for alcohol-gasoline blends. *Fuel*, 79(11), 1405–1411.
191. Kim, S., Dale, B.E. (2005) Life cycle assessment of various cropping systems utilized for producing biofuels: Bioethanol and biodiesel. *Biomass and Bioenergy*, 29(6), 426–439.
192. Hsieh, W.D., Chen, R.H., Wu, T.L., Lin, T.H. (2002) Engine performance and pollutant emission of an SI engine using ethanol-gasoline blended fuels. *Atmospheric Environment*, 36(3), 403–410.
193. He, B.Q., Shuai, S.J., Wang, J.X., He, H. (2003) The effect of ethanol blended diesel fuels on emissions from a diesel engine. *Atmospheric Environment*, 37(35), 4965–4971.
194. Taylor, A.B., Taylor, A.B., Moran, D.P., Bell, A.J., Hodgson, N.G., Myburgh, I.S., Botha, J.J. (1996) Gasoline/alcohol blends: Exhaust emission, performance and Burn-rate in multi-valve production engine. *Society of Automotive Engineers*, Topics in Alternative Fuels and Their Emissions, SP–1208.
195. Furey, R.L., Jackson, M.W. (1977) Exhaust and evaporative emissions from a Brazilian Chevrolet fuelled with ethanol-gasoline blends. *SAE paper no. 779008*.
196. Merritt, P.M., Ulmet, V., McCormick, R.L., Mitchell, W.E., Baumgard, K.J. (2005) Regulated and unregulated exhaust emissions comparison for three tier II non-road diesel engines operating on ethanol- diesel blends, *SAE paper no. 2005-01-2193*.
197. Muja, I., Toma, A., Popescu, D.C., Ivanescu, I., Stanisteanu, V. (2005) Thermodynamic study of the methanol addition to isoamylen. *Chemical Engineering and Processing*, 44(6), 645–651.
198. Islas, J., Manzini, F., Masera, O. (2007) A prospective study of bioenergy use in Mexico. *Energy*, 32(12), 2306–2320.
199. Lopes, T.J., Bender, D.A. (1998) Nonpoint sources of volatile organic compounds in urban areas – relative importance of land surfaces and air. *Environmental Pollution*, 101(2), 221–230.
200. Ancilloti, F., Fattore, V. (1998) Oxygenate fuels: Market expansion and catalytic aspects of synthesis. *Fuel Processing Technology*, 57, 163–194.
201. Gressel, J. (2008) Transgenics are imperative for biofuel crops. *Plant Science*, 174, 246–263.
202. Van Eijck, J., Romijn, H. (2008) Prospects for Jatropha biofuels in Tanzania: An analysis with Strategic Niche Management. *Energy Policy*, 36, 311–325.
203. Francis, G., Edinger, R., Becker, K. (2005) A concept for simultaneous wasteland reclamation, fuel production, and socio-economic development in degraded areas in India: Need, potential and perspectives of Jatropha plantations. *Natural Resources Forum*, 29, 12–24.
204. Gubitz, G.M., Mittelbach, M., Trabi, M.L. (1998) Exploitation of the tropical oil seed plant Jatropha curcas L. *Bioresource Technology*, 67, 73–82.
205. Luque, R., Herrero-Davila, L., Campelo, J.M., Clark, J.H., Hidalgo, J.M., Luna, D., Marinas, J.M., Romero, A.A. (2008) Biofuels: A technological perspective. *Energy and Environmental Science*, 1, 542–564.
206. Lai, C.C., Zullaikah, S.S., Vali, R., Ju, Y.H. (2005) Lipase-catalyzed production of biodiesel from rice bran oil. *Journal of Chemical Technology and Biotechnology*, 80, 331–337.
207. Molina Grima, E., Belarbi, E.H., Acien Fernandez, F.G., Robles Medina, A., Chisti, Y. (2003) Recovery of microalgal biomass and metabolites: Process options and economics. *Biotechnology Advances*, 20, 491–515.
208. Dijkstra, A.J. (2006) Revisiting the formation of trans isomers during partial hydrogenation of triacylglycerol oils. *European Journal of Lipid Science and Technology*, 108, 249–264.
209. Vosloo, A.C. (2001) Fischer-Tropsch: A futuristic view. *Fuel Processing Technology*, 71, 149–155.